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Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

Final Report

Phase I SBIR # 90-13

DAAL 04-90-C-0013

4-15-91

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NOTICE

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Statement A per telecon Robert Morrissey
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Final Report

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Report Submitted to:

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Contract # DAAL04-90-C-0013

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Date of Report:

April 15, 1991

SUMMARY:

The following is the Final Report for contract DAAL04-90-C-0013 submitted to the USAMTL in Watertown, MA. The report describes the accomplishments achieved throughout the 6 month Phase I program started on July 16, 1990. During this period experiments were conducted to demonstrate the feasibility of a novel optical fiber based composite cure monitoring technique. Preliminary investigations were conducted using a fast cure, industrial grade epoxy in a neat resin environment. These investigations not only verified basic principles of operation, but also suggested methods to improve monitor performance. Subsequent neat resin tests were demonstrated using a more common composite resin, Hercules' 3501-6 material. A neat resin cure monitoring station, which allowed repeatable cure monitoring results, was developed. A cure monitor assembly which addressed practical feasibility issues, was also developed. This assembly made it possible to interface the relatively fragile resin fiber elements with standard all-silica lead fibers without requiring micro-positioning equipment for alignment. In order to simplify the data acquisition process during the cure monitoring cycle, a PC-Basic routine was written which allowed continuous retrieval of data from a multi-channel optical meter as well as conventional thermocouples. This routine was used to perform cure monitoring measurements on Hercules 3501-6/AS4 composite coupons. Normalized Transmitted Power (NTP) as a function of cure was monitored and showed correlation to the neat resin experiments conducted earlier. Although an embeddable Liquid Core Fiber (LCF) temperature monitor was developed and optimized for operation at 175 °C (the cure temperature of the Hercules 3501-6 resin) as proposed, initial experiments indicate that the impact of fluctuating temperature on cure monitor performance is negligible. Furthermore, resin pressure changes are not anticipated to affect the fiber optic cure monitor, which in conjunction with the monitor's relative insensitivity to temperature fluctuations, could lead to a completely non intrusive, in situ cure monitoring technique. Preliminary suggestions for further improvements and follow-up Phase II efforts are also addressed.

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

(Final Report)

1.) INTRODUCTION:

1.1) Report Logistics:

This Final Report summarizes the accomplishments achieved on SBIR Phase I contract # DAAL04-90-C-0013 titled "Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials" which began on July 16, 1990. The objective of the program was to demonstrate the feasibility of optical fiber sensors for monitoring the cure state of composite materials. Progress made during the six month program has been reported in detail on a monthly basis through monthly Technical Status Reports. These are attached in Appendices A-E, and will be referred to throughout this report. In order to avoid redundancy, only key accomplishments from these reports will be extracted, while detailed information can be found in the respective Appendix sections. It is strongly suggested that the reader look at these sections if he/she has not been receiving the monthly reports periodically.

1.2) Phase I Program Goals:

Phase I program goals were summarized in the SBIR Phase I proposal submitted to USAMTL in January of 1990. These goals consisted of developing, testing, and implementing an optical fiber based cure monitoring technique which would allow the determination of the state of cure of an organic matrix composite during its fabrication, while minimizing the effects on composite integrity due to embedding the required sensing elements. It was proposed to utilize an optical fiber waveguide made out of the composite resin material as the sensing element. This element would be embedded within the composite such that incorporation of "foreign" sensor elements such as conventional electro-resistive gages could be avoided. While the principle of operation is outlined in Section 2.1, the basic concept consists of choosing the sensor waveguide material to be the same as the resin of the composite structure. Since these resins are usually somewhat optically transparent, a probe signal can be launched through a fiber made out of the resin. As will be shown, the intensity of this signal is directly related to the state of cure of the composite.

2.) BACKGROUND:

2.1) Principle of Operation:

The organic matrix composite cure monitor is based on correlating the resin refractive index to its state of cure. The refractive index change of the resin is monitored using optical fiber waveguide techniques. A waveguide fiber is manufactured using the resin material of the organic matrix composite itself. Different methods to achieve desired waveguide diameter and uniformity exist,

and the optimum approach will be presented. After insuring that the resin fibers have been allowed to cure completely, they are embedded in the resin to be monitored. An optical signal launched into the cured resin fiber will excite a number, M, of optical "modes" given approximately by:

$$M = \frac{v^2}{2}, \tag{1}$$

where v, the waveguide normalized frequency, is given by :

$$v = \frac{2\pi \mathbf{a}}{\lambda}(n_1^2 - n_2^2)^{\frac{1}{2}}. \tag{2}$$

In Equation (2), **a** is the resin fiber diameter, λ the operating wavelength, n_1 the refractive index of the cured resin fiber, and n_2 the refractive index of the resin to be monitored. As the resin cures, the optical power, P, transmitted through the resin fiber changes according to:

$$\frac{dP}{dt} = \frac{dP}{dn_2}\frac{dn_2}{dt}, \tag{3}$$

where dP/dn_2 is assumed to be proportional to dM/dn_2, that is:

$$\frac{dP}{dn_2} = K\frac{dM}{dn_2}. \tag{4}$$

K depends on several factors including optical launch conditions into the lead fiber, fiber interaction length, cure temperature, and cure pressure. As will be explained in the experimental section, a reference signal, P_{ref}, will be tapped from the optical source to compensate for source output drift. The Normalized Transmitted Power (NTP), which will be related to the state of cure, is given by:

$$NTP = \frac{P}{P_{ref}}. \tag{5}$$

2.2) Technical Approach:

The proposed technical approach consisted of following a sequential development path which included the items listed below:

- Demonstrate the principle of operation first with an off-the-shelf, fast cure epoxy.
- Proceed experimentation with a more typical composite resin used in the composites industry.
- Determine that resin's optimum operating wavelength, pre-monitoring conditioning, and fiber fabrication processes.
- Test the cure monitoring techniques with the neat resin for calibration.
- Finally, test the cure monitoring techniques with sample composite specimens.

The approach that was taken to accomplish the above items is given in detail in Appendices A-E. The experiment procedures and results are summarized in Section 3 below.

3.) PHASE I EXPERIMENT PROCEDURES & RESULTS:

3.1) *The Fast Cure, Biphenol-Diglycidylether (BD) Resin System:*

An industrial grade, fast cure BD resin system from Devcon, Inc. was used to demonstrate the cure monitor principle of operation. The experiments conducted consisted of a) resin preparation, b) fiber fabrication, c) operating wavelength determination, d) neat resin cure monitoring, and e) comparison with Fourier Transform Infra-Red (FTIR) spectroscopic methods. Details on experiment procedures can be found in Appendix A of this report. The key results consist of the following:

- Resin fibers could be fabricated such that their outer diameters matched that of standard all-silica optical fibers (200 - 600 μm).
- The operating wavelength could be optimized by performing spectral attenuation on the resin to be used for cure monitoring.
- Cure monitoring on the neat resin (which in this case did not require a heating process) was performed, and was shown to allow improvements in sensitivity by varying interaction length and launch conditions.
- Good correlation between the fiber optic method and conventional FTIR methods was observed.

Data supporting the above results is given in Figures 1-4 of Appendix A.

3.2) The Hercules 3501-6 Thermoset Resin System:

Resin preparation, fiber fabrication, and operating wavelength selection procedures are outlined in Sections 3.2.1 - 3.2.3 of Appendix A. Improvements to these procedures are given in Section 3.1.1 ("The Modified Resin Fiber Fabrication Process")of Appendix B. In summary, the Hercules 3501-6 resin was preconditioned at 125 °C to remove air bubbles, the uncured resin was drawn into a silicone mold, was allowed to cure at approximately 175 °C, and was subsequently removed from the mold by splitting it open. The operating wavelength was chosen to be 816 nm provided

by a 3 mW output power CW solid state laser (see Section 3.2.3 of Appendix A). A cure monitor assembly was developed to eliminate the need for micropositioning equipment (see Section 3.1.2 of Appendix B) and a cure monitoring station was designed and manufactured to perform preliminary experiments on Hercules 3501-6 neat resin samples (see Section 3.1.3 of Appendix B).

3.3) Hercules 3501-6 Neat Resin Cure Monitoring:

Neat resin samples were tested as described in Section 3.1 of Appendix C. A heating block assembly was used to obtain repeatable experiment set-ups (see Figure 1 of Appendix C), and results of Normalized Transmitted Power (NTP) as a function of time were achieved for 508 μm diameter resin fibers ranging in length from 2.6 to 7.8 cm. Repeatability was demonstrated after temporally normalizing the NTP to the point in time at which transmitted power had reached a maximum (see Figure 5 of Appendix C). Resin rate of cure was shown to be best determined by numerically differentiating the NTP (see Figures 2 and 3 of Appendix D). Thus, the rate of cure as a function of time could be found. The resultant curve approached a value of zero as the cure cycle was nearing completion.

3.4) Hot Press Cure Monitoring - Experiment Procedures:

A 1 ton Carver 15 x 15 cm hot press was modified to allow cure monitoring on Hercules 3501-6/AS4 composite coupons (see Section 3.3 of Appendix D). 32 plies of the composite prepreg material were placed in an aluminum mold such that the cure monitoring resin fiber was sandwiched between the 12th and 13th plies. Although the resin fiber diameter was still relatively large (~508 μm) compared to the diameter of the graphite fibers of the composite, it was not possible to distinguish the location of the fiber through simple visual inspection. A photomicrograph of the coupon crossection (see Figure 5 of Appendix E) revealed the exact placement of the resin fiber within the composite coupon. The 508 μm diameter of the resin fiber effectively resulted in a resin rich region within the composite which must be minimized in the future by developing methods to fabricate smaller diameter resin fibers.

3.5) Hot Press Cure Monitoring - Experiment Results:

Figure 2 of Appendix E shows the results of the hot press composite cure monitoring experiments. During the preheat cycle at approximately 125 °C the decrease in NTP is relatively small. Once temperature is increased to approximately 175 °C the NTP starts decreasing rapidly. Figure 4 of Appendix E again shows that numerical differentiation of the NTP results in a signal which approaches zero as the specimen cures. This yields a direct composite cure state criterion which can be used for real time cure process control purposes. For example, once |dNTP/dt| falls

below a certain value, one might safely assume that the composite has cured, and begin bringing the specimen back to room temperature.

3.6) Impact of Fluctuating Temperature and Pressure:

Although the original SBIR Phase I solicitation asked for temperature and pressure monitors to establish the state of cure of a composite, it is our belief that these monitors may not be required with the proposed fiber optic cure monitor. This assumes that the impact of fluctuating temperature and/or pressure within the composite during fabrication is minimal if not negligible on the monitor's output. Fluctuating temperature will cause a change in resin fiber density, thus causing the NTP to vary accordingly. These variations in NTP, however, are not significant and do not seem to be detrimental to the system's accuracy. A temperature fluctuation of approximately +/- 5 °C about 175 °C, for example, resulted in minimum impact on NTP and dNTP/dt (see Figures 2 and 3 of Appendix E). Similarly, we have not seen sensitivity to pressure fluctuations within the composite during cure. This is probably due to the high stiffness of the 508 μm diameter resin fiber which prevents microbending effects. These effects could be more significant as the fiber diameter is reduced in the future.

3.7) Computer Interfacing:

Software has been developed to acquire and store the reference and measurement signals from the optometer through a GPIB interface, as well as track the temperature of the composite through an A/D board (see Section 3.1 of Appendix D). A listing of the software written in PC Basic is also given in Appendix D.

4.) PHASE II FOLLOW-UP EFFORTS:

The experimental results of the Phase I project have established the direction of future development regarding the proposed fiber optic cure monitor. Several crucial factors will have to be included and analyzed during subsequent Phase II follow-up efforts. Immediate suggestions for Phase II development, which will be addressed in more detail in a pending Phase II proposal, include a) neat resin preparation before resin fiber fabrication, b) improved resin fiber fabrication techniques, c) resin fiber embedding and interaction with the composite, d) interpretation of the monitor data and subsequent process control, e) impact of the cure monitor on composite characteristics, and f) use of the developed monitor not only for cure but also post cure sensing applications.

4.1) Neat Resin Preparation:

The resin currently used for making the cure monitor resin fibers is standard grade Hercules 3501-6 resin material. The material, as currently received from the supplier, has not undergone any special purification treatment, nor has emphasis been placed on degasing/de-airing the material. Considering that in the future longer length (> 1 m) fibers may be needed, it will be necessary to look at techniques which will insure the highest optical transmission coefficients. With a typical monitoring system dynamic range of approximately 30 dB, and a maximum resin fiber length of, let's say 10 m, the loss of the resin material after purification and de-airing would have to be less than 3 dB/m. Whether such a low material loss is possible will have to be determined.

4.2) Resin Fiber Fabrication:

The methods currently used to fabricate the resin fibers are adequate for demonstration of feasibility. However limitations on minimum fiber diameter, maximum fiber length, and presence of fiber contaminants still exist. Since a mold technique is used to make the fibers, the removal of the fibers from the mold after curing becomes extremely difficult for fibers having a diameter of less than 300 μm. Removal, and also filling of the mold with the resin material currently limit the maximum achievable fiber length to approximately 15 cm. Handling of the cured resin fiber places contaminants on its surface, and can cause surface scratches which will negatively affect its transmission characteristics. It is therefore proposed to look at alternate fiber fabrication techniques. These include hollow capillary tube filling methods in conjunction with electrolysis or chemical etching for subsequent capillary tube removal. These methods are already being addressed in our labs and may provide the answer to making fibers with diameters < 100 μm and lengths > 1 m.

4.3) Resin Fiber Embedding:

Further focus on placement of the resin fiber within the composite is also proposed. As the fiber diameter decreases, proper placement to minimize fiber losses due to microbending will be necessary. At this point the fiber diameter is still large enough (508 μm) that microbending due to the pressure of the graphite fibers against the fiber surface is expected to be minimal. The effect of microbending however will become an issue as the diameter of the resin fiber approaches that of the composite graphite fibers. Special fiber lay-ups may be necessary to minimize microbending losses.

4.4) Process Control:

Once fully understood, the fiber optic cure monitor will provide cure state information which can be used to control the cure process. Complete understanding of the monitor includes

establishing cure criteria for various fiber types, lengths, diameters, and resin types. Once these criteria exist, real time feedback loops can be implemented to adjust cure conditions accordingly. These conditions include cure pressure, temperature, and time all of which need to be optimized for an efficient, cost effective process.

4.5) Cure Monitor Impact on the Composite:

It is also advised to perform a detailed test program which will address the impact of the embedded resin fibers on composite coupon strength and fatigue. Once an optimum resin fiber/fiber lay-up combination has been determined, a rigorous test program should be conducted. This program should include traditional tensile and flexural strength, as well as fatigue/aging testing. Emphasis will also be placed on resin fiber bonding to the composite, since it is expected to play a major role in not only preserving the integrity of the composite, but also in using the fiber for sensing applications after the composite is manufactured.

4.6) Post Cure Sensing Applications:

In the original SBIR solicitation an interest in using the embedded cure monitor for post cure process sensing applications was expressed. Preliminary composite coupon inspections in our laboratories indicate that this could be feasible; optical transmission loss of the resin fiber even after the cure process is completed seems to be low enough to allow visual detection of ambient, uncollimated light through a 4.5 cm wide specimen. This suggests that the embedded cure monitor fiber, which has already blended in with the composite structure, provides a light path for an optical probe signal at a particular wavelength. This light path can therefore be used to sense parameters during the lifetime of the composite. Such parameters include strain, temperature, and pressure.

5.) CONCLUSIONS:

The data in this report shows that the proposed fiber optic composite cure monitor has successfully been tested for feasibility. Experiments conducted on both Hercules 3501-6 neat resin as well as AS4 prepreg specimens have yielded reliable and repeatable data. Experiments using these composite resins and prepreg materials demonstrate the practicality of the proposed approach. Prototype monitoring stations which not only include all necessary optical components, but also related PC interface software, have been manufactured and are available for subsequent development and optimization

APPENDIX A

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

Monthly Technical Status Report (7/16/90 - 8/14/90)

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Contract # DAAL04-90-C-0013

Author of Report:

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Date of Report:

August 15, 1990

SUMMARY:

The following is the first monthly technical status report regarding contract DAAL04-90-C-0013 submitted to the USAMTL in Watertown, MA. The report describes the activities and progress during the first month of this project as pertaining to the submitted SBIR Phase 1 proposal ("Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials"). According to this proposal, a major part of the first task, developing the fiber optic cure monitor, was scheduled to be accomplished. Toward this objective, we have investigated first, a low loss, fast cure industrial epoxy, and secondly, a commercially available thermoset resin supplied by Hercules (3501-6). The fast cure epoxy has allowed us to establish operating wavelength selection procedures, determining the feasibility of using and embedding resin optical waveguides, demonstrating the effect of resin fiber length and launch conditions on monitor sensitivity, and comparing the fiber optic sensor results to conventional FTIR methods. As stated, we have also looked at a more typical resin, Hercules 3501-6, which is commonly used in the composites industry. This resin was slightly more difficult to work with since the fiber fabrication process as well as the cure process are more complicated than those of the fast cure epoxy. We have determined a suitable resin preparation process, and a technique to fabricate 300-600 μm diameter resin fibers having lengths greater than 5 cm, as well as developed a special cure monitoring set-up for these thermoset resins. Verification of the sensitivity improvement techniques used with the fast cure epoxy is anticipated to occur within the next two weeks, after which the temperature monitor development will begin (Task 2).

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

1.) INTRODUCTION:

The following document is aimed at reporting progress achieved on contract DAAL04-90-C-0013 during the period of 7/16/90 through 8/14/90. A majority of the first task of our SBIR Phase 1 proposal titled "Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials" has been completed as scheduled. The work performed during this first month involved developing the resin cure monitor. Two resins were studied: a fast cure, low loss industrial grade Biphenol-Diglycidylether and a commercially available thermoset resin used commonly in the composites industry. The industrial grade resin system was used to demonstrate the principle of our proposed approach. This resin system has the following advantages over the thermosets: 1.) The resin cures within a matter of minutes without requiring a heating process, thus making the resin fiber fabrication and cure monitoring process easier, and 2.) The resin is relatively transparent at visible wavelengths (633 nm), making optical alignment and detection easier. Once the principle was demonstrated with this fast cure resin system, we proceeded to perform experiments using the Hercules 3501-6 material. The steps used to prepare the resins, fabricate the fibers, and perform the cure monitoring measurements for both resins are described below.

2.) BACKGROUND:

The cure monitor is based on the fact that during the cure process a resin experiences a change in refractive index. By fabricating an optical fiber out of the resin to be monitored, and letting it cure completely, it is possible to embed that fiber in the uncured resin material. The cure state of that material can be determined by correlating the intensity change of an optical signal launched into the embedded fiber to ongoing chemical cure reactions. The main advantage of this technique is that the embedded sensor "blends" in with the composite since it is made out of the same material, and is therefore anticipated to minimize degradation of the integrity of the finished composite structure. More detailed information on this principle was given in our SBIR Phase 1 proposal and should be used as reference [1]. The basic objective of Task 1 of this project is to verify this principle. We started out by looking at a Biphenol-Diglycidylether as a candidate resin system.

3.) EXPERIMENTS:

3.1) The Biphenol-Diglycidylether (BD) Resin System:

The BD resin system (supplied by Devcon, Inc.) is an industrial grade fast cure epoxy not typically used in composite structures. Nonetheless, this resin system allowed us to conduct preliminary experiments as described below to demonstrate feasibility. These experiments consisted of a) Resin Preparation, b) Fiber Fabrication, c) Determination of Operating Wavelength, and d) Cure Monitoring.

3.1.1) Resin Preparation:

The BD resin system reaches its 90% cure state within a matter of 15 minutes. Thus, the two component resin cannot efficiently be evacuated to remove suspended air due to mixing of the components. We proceeded by minimizing suspended air pockets through slow manual stirring using small amounts (< 10 g) of both components (Resin and Hardener). As was observed later, the quality (i.e., signal attenuation) of the fibers to be fabricated out of the mixed resin strongly depended on the number of air pockets per given fiber length. Preparation of the BD system did not require any heating process. This dual component epoxy does, however, exhibit exothermic behavior typical of this class of resin.

3.1.2) Fiber Fabrication:

The fabrication of the resin fibers was relatively uncomplicated. Just prior to the gel point, small quantities of the material were lifted out of the mixing dish using a small wooden rod causing a thin strand of material to be suspended between the material in the dish and the wooden rod. This strand was stretched until the desired diameter was achieved. Since we anticipated using 200 μm core lead fibers to launch the optical signal into the resin waveguide, a diameter of approximately 200 μm was targeted for the input end of the resin fiber. The output end of the resin fiber was usually 20 - 50 μm smaller in diameter due to the pulling/stretching process (this is a disadvantage of this process). The lengths of the fabricated BD fibers varied between 4 and 15 cm, while the air pocket content was typically below 0.25 cm^{-1}. Care was taken to avoid contact with the resin fiber, even after curing was completed.

3.1.3) Determination of Operating Wavelength:

To optimize the performance of the proposed cure monitor it was necessary to develop a technique which would allow finding the wavelength(s) at which attenuation and loss are minimized. One suitable approach consisted of using the fabricated resin fibers and characterizing them with a commercially available fiber spectrum analyzer (FOA 2000 by Photon Kinetics). Attenuation was measured from 600 to 1600 nm in 10 nm steps with results as shown in Figure 1

The spectral plot shows that for the approximately 4.0 cm long fiber, an attenuation of less than 1.0 dB can be expected at visible (633 nm).and IR (800 - 1100 nm) wavelengths.

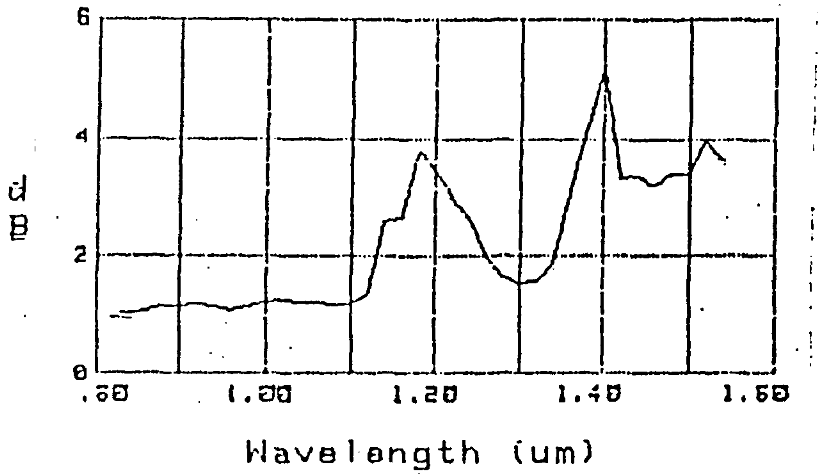

Figure 1: Spectral Attenuation Graph for the Biphenol-Diglycidylether Resin.

3.1.4) Cure Monitoring:

3.1.4.1) The Transmissive Mode Cure Monitor:

Figure 2 shows the set-up of the transmissive mode cure monitor for th BD resin system. It consists of a 633 nm Helium Neon, 5 mW output power gas laser source, a 4x, 0.2 NA collimating lens, a fiber holder, 200/230 µm Hard Clad Silica (HCS) lead fibers from Ensign Bickford, a radiometric silicon detector, and an analog optical power meter. The cured resin fibers were placed on a glass microscope slide, attached in place with adhesive tape, and aligned with respect to the lead fibers using micropositioners. Interaction lengths ranging from 4.2 to 12.6 cm were used to determine the effect of interaction length on monitor sensitivity.

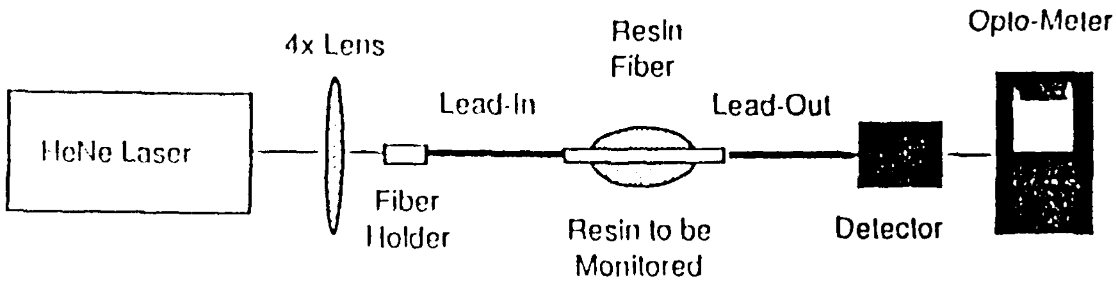

Figure 2: The Transmissive Mode Epoxy Cure Monitoring Set Up.

As can be seen from the plot in Figure 3, the decay of normalized transmitted power decays much more rapidly for the longer interaction length fibers. Also interesting is the fact that, after normalizing the slopes of the curves in Figure 3 to the fibers' respective lengths, agreement was found with the rate of cure determined using infrared spectroscopic methods. This indicates that, at least for this particular resin system, the proposed approach yields cure monitoring results which can be correlated to the results obtained through conventional, non-in-situ techniques.

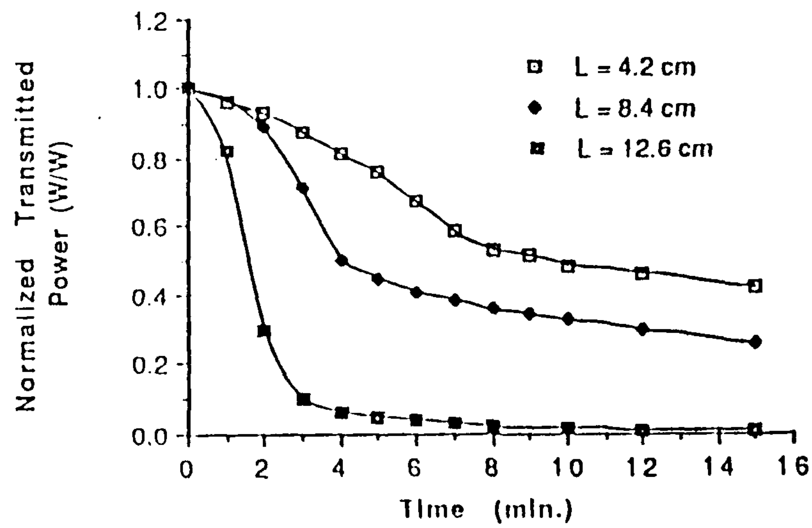

Figure 3: Graph Showing the Effects of Interaction Length on Cure Monitor Sensitivity.

3.1.4.2) Higher Order Mode Launch:

In anticipation of a need for improved sensitivity and dynamic range we have conducted several experiments. These experiments have included excitation of primarily "higher order" optical modes within the embedded resin fiber. These modes can be envisioned from an optical ray theory point of view as rays propagating at a steeper angle with respect to the fiber axis. Thus, unlike the rays which propagate straight down the center of the fiber parallel to its axis, the higher order modes experience much more interaction at the fiber core/cladding interface (the interface between the cured resin fiber and the uncured resin to be monitored). The higher order mode launch for the BD resin system was accomplished by focusing the input optical signal into the input lead fiber at an angle of approximately 15 °. Figure 4 shows how the dynamic range (defined as 10 times the log of the maximum normalized transmitted power over the minimum normalized

transmitted power) can be improved by a factor of at least 3 for both trial A and B. Both trials were performed using a 4 cm BD resin fiber.

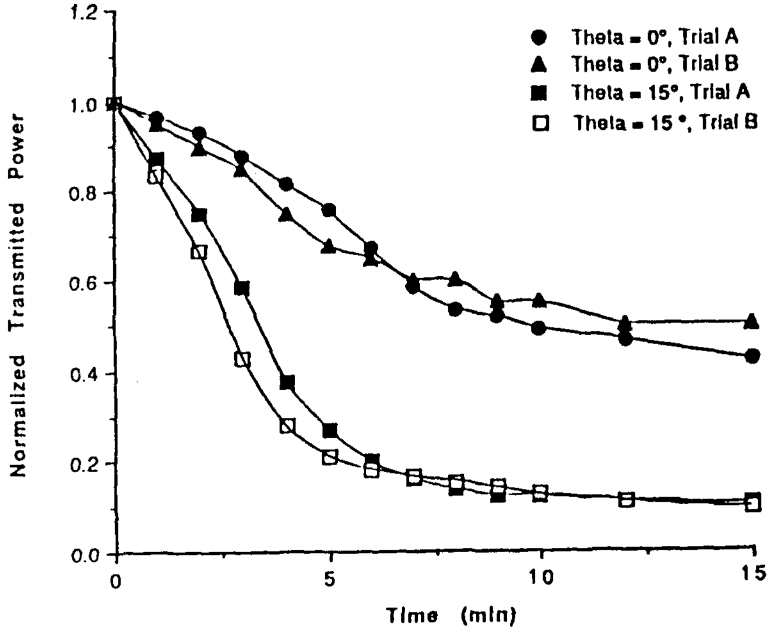

Figure 4: Graph Showing the Effects of a Higher Order Mode Launch Set-Up.

3.2) The Hercules 3501-6 Thermoset Resin System:

The Hercules 3501-6 resin, more commonly used for composites, required a significant amount of modifications and adaptations in most if not all of the experiments. This was mainly due to the fact that a) The resin needs to be heated beyond 150 °C to cure, and b) The cure process may take over 2 hours to be completed. The impact of these two factors becomes evident in Sections 3.2.1 - 3.2.4.

3.2.1) Resin Preparation:

Unlike the BD resin system, the Hercules 3501-6 resin system (like many other thermoset systems) is a single component material which is typically stored at very cold temperatures (< -10 °C) to avoid the curing process. The material usually contains a large amount of air as supplied by the manufacturer, and needs to be "de-aired" before proceeding to the fiber fabrication process. We found it to be of benefit to avoid having to evacuate the resin to accomplish this goal since the evacuation process is relatively slow and not always very effective. Our approach entailed placing small amounts of the cold resin straight out of the freezer, still in "crystalline" form, into 30 ml glass beakers. After the temperature was raised to approximately 100-125 °C for half an hour using a 3500 cm^3 oven with a glass window for visual inspection, the viscosity of the material would decrease enough to allow most if not all of the air bubbles to rise to the top and out of the material. It was very important to keep the depth of the resin material within the beaker to a minimum (< 0.5

cm) to allow the air bubbles to surface before the material cured and became more viscous. Once most of the air was out of the resin and the viscosity of the resin was very low (i.e., just prior to its gel point), the fiber fabrication process could be performed.

3.2.2) Fiber Fabrication:

It was decided that the draw process used to fabricate the BD resin fibers would not be practical with the 3501-6 material. Not only was this process found to be extremely difficult to be performed at elevated temperatures, but also inconsistent in that the quality of the resin fibers depended strongly on the patience and "steady hands" of the operator. We therefore opted to pursue molding the fibers inside of a Silicone rubber (Sylgard 184 by Dow-Corning) mold. The mold was fabricated by embedding 300 to 640 μm stainless steel rods in the rubber material, letting the material cure, and then withdrawing the rods leaving behind 5-6 cm long, uniform diameter (recall that the BD fibers were tapered!) cavities. To fill the mold with the prepared resin material, 365 μm outer diameter, 150 μm inner diameter polyimide coated silica capillaries from Polymicro Technologies were guided into one end of the mold cavities. The mold was lowered into the low viscosity 3501-6 resin at approximately 125 °C and a vacuum was applied to the capillaries. This caused the resin to be succtioned into the Sylgard mold cavities. Once the resin was succtioned all the way to the top of the mold cavities temperature was increased to 175-200 °C while vacuum was still applied.The mold was kept at that temperature for 2 hours (both the Sylgard 184 and the polyimide coated capillaries can easily withstand> 250°C) to let the resin cure. The cured fibers were removed from the mold at room temperature by slicing the mold with a sharp blade. A photomicrograph of finished 300 μm and 640 μm 3501-6 fibers is shown in Figure 5 (80 X Magnification) .

3.2.3) Determination of Operating Wavelength:

The operating wavelength selection procedure was the same as the one used for the BD fibers. The FOA 2000 fiber spectrum analyzer was used to generate the plot in Figure 6. Again, a low-loss plateau can be observed at 800 to 1100 nm, however , below 800 nm attenuation starts to increase. We were therefore inclined to use a 816 nm, 3 mW output power CW solid state laser for subsequent experiments. At this wavelength we measured a resin fiber attenuation of a 5.2 cm 640 μm fiber at approximately 12 dB. Considering that a significant amount of this loss is due to the lead-out to resin fiber diameter mismatch (recall that the lead-out fiber core diameter is 200 μm), it is anticipated that losses with matched diameter fibers might be less than 1 dB/cm. This must still be verified.

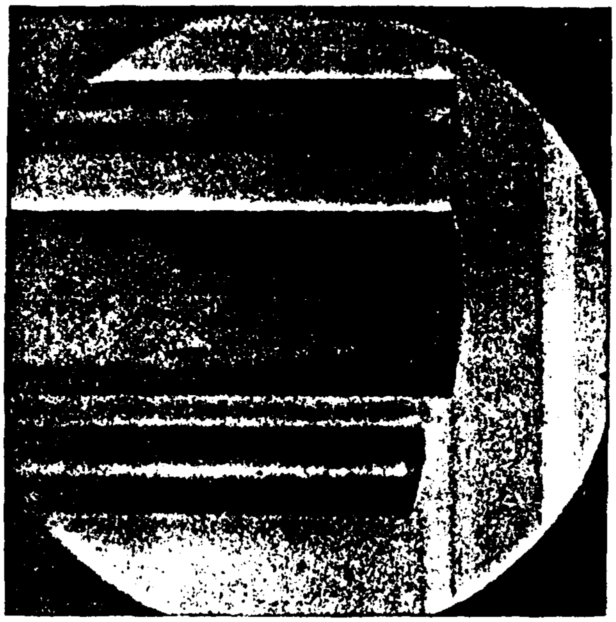

Figure 5: Photomicrograph Showing 300 μm (Bottom) and 640 μm (Middle) Hercules 3501-6 Fibers Compared to a 240 μm Glass Fiber (Top).

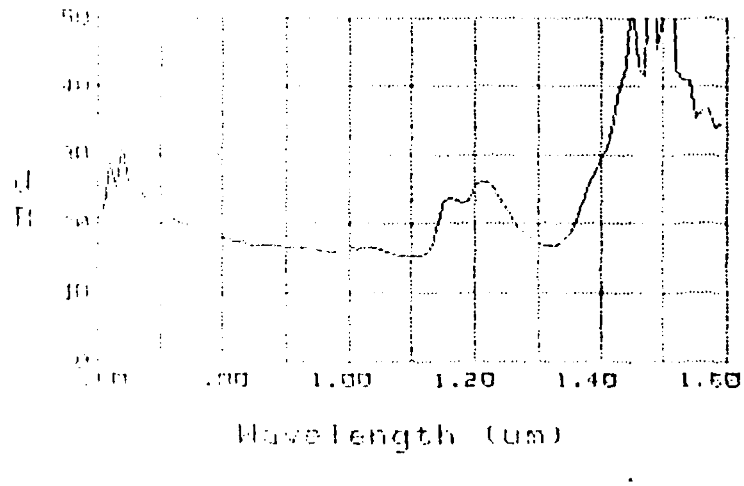

Figure 6: Spectral Attenuation for the Hercules 3501-6 Thermoset Resin.

3.2.4) Cure Monitoring:

The cure monitoring experiments performed with the 3501-6 resin fibers have not yet been completed and are scheduled to occur in the next two weeks. To date the monitoring station, which is very different from the BD resin set-up due to the need for resin heating, has been built and is drawn schematically in Figure 7. It includes the 816 nm, 3 mW output CW laser which launches its optical signal into a special tap-off coupler that splits the input signal at a 95/5 % ratio.

The 5% signal is sent straight to a Germanium detector (#1) and is used as a reference to track laser drift (this is important since the monitoring process is expected to last several hours). The 95% output of the tap-off coupler is sent to the input of the resin fiber via a 200/240 μm polyimide coated all-silica lead fiber. The resin fiber is suspended in a 4 cm long pool formed by a drilled-out aluminum block protected from the resin by heat resistant Kapton tape (by DuPont). At least 0.5 cm of resin fiber will remain outside of the aluminum block at each end to be accessed by the lead-in and lead-out fibers. The aluminum block is mounted rigidly to an optical bench between two micropositioners which align the lead fibers to the resin fiber. The block is heated with a firing rod that is positioned directly underneath the resin pool. A thermocouple monitors the block temperature and controls the current to the firing rod. A microscope is mounted right above the aluminum block for visual inspection. The lead-out fiber is connected to a second Germanium detector (#2). Both detectors are hooked to a United Technologies S390 Optometer which allows the reference and measurement signals to be subtracted from each other continuously to account for laser drift. The Optometer also provides signal averaging capabilities and can be accessed through a GPIB interface port.

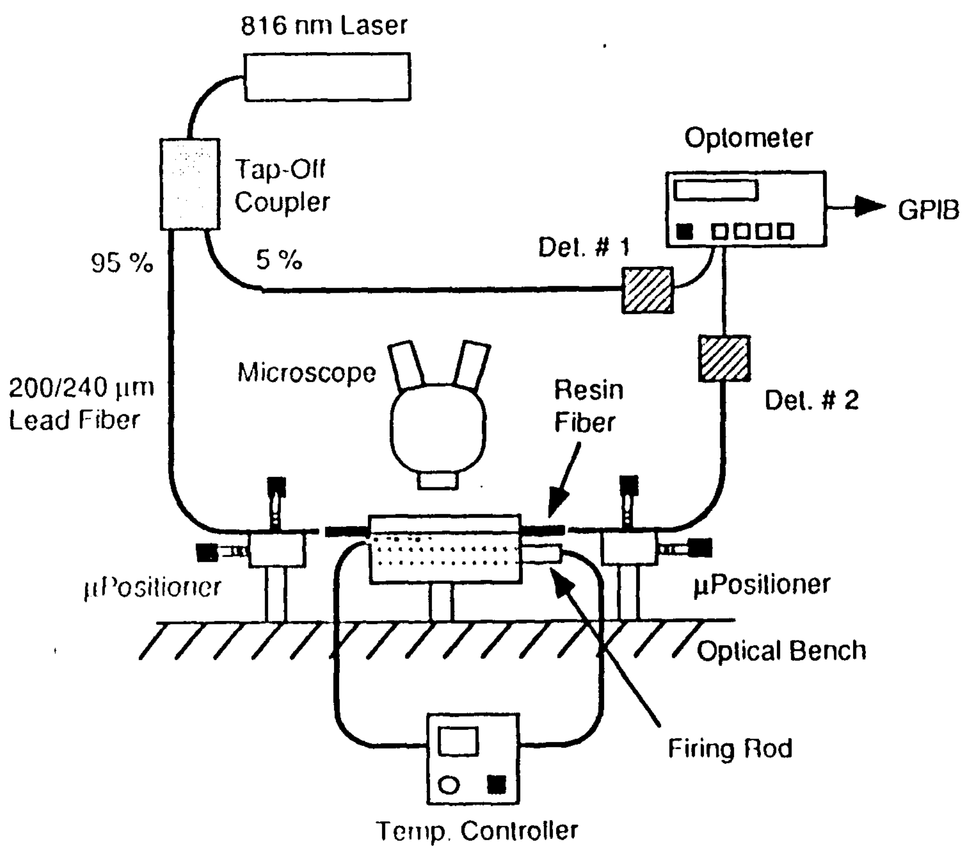

Figure 7: Epoxy Cure Monitoring Set-Up for the Hercules 3501-6 Resin System.

With the above set-up we have already achieved transmitted power levels of 300 μW through the 5 cm resin fiber (w/o surrounding resin). Given a minimum detectable signal level of approximately 30 nW, this implies possible measurement dynamic ranges of up to 40 dB. However, a more realistic dynamic range figure might be placed at approximately 30 dB due to the losses incurred as the resin is poured around the fiber.

4.) UPCOMING TASKS:

During the second month of this contract we will continue with the Hercules 3501-6 experiments. Specifically, we will pursue the fabrication of smaller diameter (200 -300 μm), longer length (5 - 10 cm) resin fibers. We will also complete all non-temperature compensated cure monitoring experiments (this includes determining the effects of varying interaction length and launch angle) and begin identifying the effects of refractive index changes due to temperature fluctuations of the surrounding uncured resin. The latter entails developing the embedded fiber optic temperature sensor suggested in our SBIR Phase 1 proposal.

5.) CONCLUSIONS:

In the period from July 16 to August 14, 1990 we have accomplished the following: a) A fast cure industrial grade dual component Biphenol-Diglycidylether resin was used to demonstrate the feasibility of the proposed cure monitor. Resin preparation, fiber fabrication, determination of operating wavelength, and epoxy cure monitoring experiments were conducted. b) A thermoset resin system from Hercules (3501-6) was subsequently investigated for similar experimentation and evaluation. Resin preparation and fiber fabrication processes were significantly different from those employed with the dual component epoxy. Spectral attenuation suggested an operating wavelength of 816 nm at which resin losses may eventually be as low as 1 dB/cm. Current fiber fabrication methods limit the minimum resin fiber diameter to approximately 200 - 300 μm. Future improvements to the fabrication process may bring down this value to 100 μm. Finally, an epoxy cure monitoring station has been set-up for immediate use during the next two weeks. This station should allow preliminary cure monitoring experiments using the 3501-6 material.

6.) REFERENCES:

[1] FIMOD Corp.SBIR Phase 1 Proposal "Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials", Dec. 29, 1990, pp.8 - 14.

[2] R. L. Levy, "A New Fiber Optic Sensor for Monitoring the Composite Curing Process," Poly. Mat. Sci. and Eng., Vol. 54, 1986, pp. 321 - 323.

[3] S. D. Senturia et al, "In-Situ Measurements of the Properties of Curing Systems with Microdielectrometry," J. Adhesion, Vol. 15, 1982, pp. 69 - 90.

[4] B. Fanconi et al, "Cure Monitoring for Polymer Matrix Composites," Materials Characterization for Systems Performance and Reliability, J. W. McCauly, V. Weis, Plenum Press, NY 1986, pp. 275 - 291.

APPENDIX B

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

Monthly Technical Status Report (8/15/90 - 9/10/90)

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Report Submitted to:

U.S. Army Materials Technology Laboratory
ATTN: SCLMT-MEC (PRA)
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Contract # DAAL04-90-C-0013

Author of Report:

Bernd D. Zimmermann

Date of Report:

September 11, 1990

SUMMARY:

The following is the second monthly technical status report regarding contract DAAL04-90-C-0013 submitted to the USAMTL in Watertown, MA. The report describes the activities and progress during the second month of this project as pertaining to the submitted SBIR Phase 1 proposal ("Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials"). Progress during this period includes modifications of and/or improvements to the resin cure monitor fiber fabrication process, lead-to-resin fiber coupling, and cure monitoring station. All of these efforts have allowed us to obtain preliminary cure monitoring results for the Hercules 3501-6 resin. Also investigated is a newly designed fiber optic temperature sensor which will be used to calibrate the cure monitor. The temperature sensor was fabricated and tested showing excellent sensitivity in the temperature range of interest (170 - 185 °C). Upcoming tasks include interfacing of both devices for simultaneous operation.

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

1.) INTRODUCTION:

The following document is aimed at reporting progress achieved on contract DAAL04-90-C-0013 during the period of 8/15/90 through 9/10/90. The work accomplished during this period was a continuation of the efforts reported in our first monthly technical status report (Task 1) as well as the beginning of the development of the temperature monitor discussed in our SBIR Phase 1 proposal (Task 2). Significant work has already been performed on device ruggedization and packaging, especially with the cure monitor, work which was originally scheduled to be completed during the later part of the contract. Since the last monthly report we have begun identifying and implementing detailed procedures for the cure monitor allowing us to present the first cure monitoring results for the Hercules 3501-6 resin. Also discussed are the need and to-date achievements regarding the newly developed fiber optic temperature monitor for embedded composite applications.

2. BACKGROUND:

2.1. Cure Monitor Improvements:

The principles of operation of the fiber optic cure monitor have been discussed in last month's technical status report and can also be found in the submitted SBIR Phase 1 proposal. As discussed in the first report, we had begun fabrication and implementation of the Hercules 3501-6 resin fibers. Preliminary fiber fabrication and testing methods were demonstrated, however, cure monitoring tests had not yet been performed. Several key factors had kept us from performing reliable cure monitoring results despite the fact that we had already obtained high quality resin fibers with our original fiber fabrication techniques. During this second month period we felt it was necessary to begin looking at improving the original resin fiber fabrication process to allow us to obtain more repeatable fiber yield rates. Testing of the fibers manufactured during the first month, for example, showed that fiber lengths needed to be increased, as well as fiber diameters to be decreased. As will be shown in this report, several crucial steps were necessary to increase the fiber lengths from 4 - 5 cm to 12 - 15 cm and to decrease the fiber diameter from 640 μm to 508 μm. Also observed during testing of the first few fibers was a need for an improved experimental set-up, a set-up that is described in Section 3.1.3.. This set-up included the effective elimination of two micropositioners used during the first month. This was accomplished after developing a new lead to-resin fiber interface package.

2.2. Cure Monitor Temperature Dependence:

Testing of the cure monitor also resulted in an awareness that performance of the sensor was dependant on accurate determination of resin temperature. As stated in the SBIR proposal, the refractive index of the cured resin monitoring fiber varies as a function of temperature. It is therefore necessary to compensate for temperature fluctuation induced refractive index changes with the use of a calibrated, embedded temperature sensor. This sensor must meet similar requirements as those needed to be met by the cure monitor (i.e., small size low profile, immune to EMI, and potentially useful for post fabrication sensing purposes). Although we are close to having developed such a temperature sensor, it is quite possible that the full advantages of the cure monitor are best accomplished by using the temperature sensor only as a tool to understand the exact behavior of the cure monitor. Specifically, the main objective of the cure monitor is to determine cure state during composite component fabrication without having to embed any foreign materials which might degrade the integrity of the finished component. The optical fiber temperature sensor, although small in diameter, would fall into the "foreign materials" category and could conceivably weaken the structure. We therefore hope, that the use of the embedded temperature sensor will eventually not be necessary given that an equilibrium cure temperature surrounding the resin fiber has been achieved. This temperature should be the resin manufacturer's recommended cure temperature, which in the case for the Hercules 3501-6 is approximately 178 °C. For purposes of first understanding the exact behavior of the resin cure monitor, it was therefore of advantage to develop a distributed temperature sensor placed along the resin fiber which could trigger an "alarm" at around 178 °C. Not only would this sensor then provide the temperature dependence of the cure monitor necessary for calibration, but it would also allow us to insure that the temperature immediately surrounding the resin fiber within the composite is at its recommended value.

2.3. The Embedded Temperature Sensor Concept:

The approach of the embedded fiber optic temperature sensor is relatively simple. The sensor includes a silica capillary with an outer diameter of 365 μm and an inner diameter of 150 μm. The capillary, which has a refractive index of approximately 1.458 is filled with a fluid (we used a Hydrogenated Terphenyl) with a refractive index substantially higher than that of the capillary itself. The fluid filled fiber thus behaves as a waveguide, with the fluid providing the waveguide core medium. The fluid is chosen such that its refractive index will drop below that of the silica capillary at approximately 178 °C. At this temperature waveguiding conditions will disappear and a substantial loss in transmitted optical power will be observed. The temperature, T_{crit}, at which waveguiding conditions disappear, is given by

$$T_{crit} = T_0 + \frac{1.458 - n_0}{\beta}, \tag{1}$$

where n_0 is the refractive index of the fluid at room temperature, β is the fluid thermo-optic coefficient, and T_0 is the room temperature (25 °C). By setting T_{crit} at 180 - 200 °C, and choosing a fluid with proper β and n_0, a temperature sensor which "triggers" at approximately 180 °C should be attained.

3.) EXPERIMENTS:

3.1 The Hercules 3501-6 Cure Monitor:

During the first month of this project we had demonstrated that 640 µm O.D. resin fibers, 6 cm in length could be fabricated using a fiber mold technique. However, significant losses were still seen due to the fact that a mismatch in diameters existed between the lead fibers (~ 200 µm) and the resin fibers (640 µm). In addition, we observed that, due to raising the resin fiber's temperature from 25 to 180 ° C necessary for resin cure, a relative movement between the micropositioner mounted lead fibers and resin fiber occurred. The fabricated cure monitoring fibers were also too short to allow easy access with the lead fibers. Due to the above, four immediate goals were identified and targeted for to improve the performance of the cure monitor:

- Modify the existing resin fiber fabrication process to yield longer length, smaller diameter fibers.
- Develop a lead-to-resin fiber package which will minimize the interface losses, eliminate relative fiber movement, and avoid the use of micropositioners.
- Modify the existing cure monitoring station to apply uncured resin repeatably and uniformly for calibration purposes.
- Perform cure monitoring experiments using the modified station.

3.1.1 The Modified Resin Fiber Fabrication Process:

To improve the resin fiber fabrication process we built a new fiber mold casing while still utilizing Dow Corning's Sylgard 184 as the mold material. The mold casing was machined out of aluminum with dimensions of 16 x 5 cm, capable of easily holding nine resin fibers 15 cm in length. After removal of the stainless steel rods, which were now only 508 µm in diameter, the aluminum casing was also used for the mold filling process. This was done by shortening the mold by 0.5 cm on each end after the rod removal, and filling the remaining 1 x 4.5 cm of casing space with molten Hercules 3501-6 resin. The resin was still succtioned into the Sylagard mold using small silica capillaries inserted into the mold cavities. The resin fiber cure process was also performed in the

aluminum casing. After the cure process was completed the fibers were removed from the mold as before using a sharp blade to split the mold and remove the finished 508 μm diameter fibers. Finished fiber lengths ranged from 12 to 15 cm.

3.1.2 The Lead-to-Resin Fiber Interface Package:

We decided that, in order to make the proposed cure monitoring sensor more practical, it would be advantageous to eliminate the need for micropositioners to align the lead fibers with the resin fiber. It also seemed logical to more closely match the diameters of the lead fibers to that of the resin fiber. Since 508 μm seemed to be a reasonable resin fiber diameter from a handling point of view, we opted to use 400/480/510 μm lead fibers which we aligned to the resin fiber using a 530 μm I.D., 700 μm O.D. polyimide coated glass capillary of ~ 1 cm length. The glass capillary was filled with a U.V. curable index matching elastomer, and ruggedized by housing it in a 1.5 mm O.D., 1.5 cm long glass tube also filled with the U.V. curable elastomer. After the elastomer was cured with a U.V. gun, the lead fibers would be permanently aligned with the resin fiber. Standard ST connectors were attached to the free ends of the lead fibers to complete the cure monitor assembly (See Figure 1).

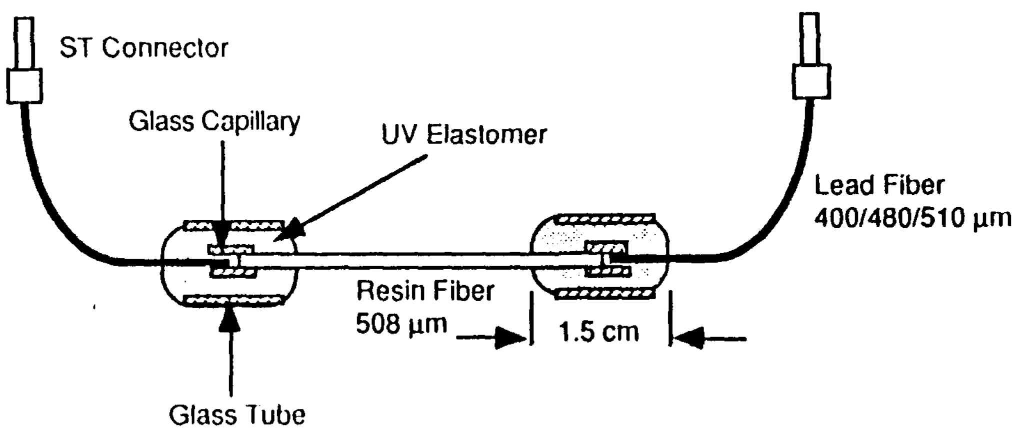

Figure 1: The Epoxy Cure Monitor Assembly for Hercules 3501-6 Resin.

3.1 3. The Modified Epoxy Cure Monitoring Station:

In anticipation of future composite coupon cure monitoring experiments, we decided to modify the existing cure monitoring station to simulate the press or autoclave process as much as possible. The elimination of micropositioners certainly helped in that respect. Another modification includes the use of 700 μm stainless steel tubes slipped over the 510 μm O.D. lead fibers to position the fibers in the resin pool, and at the same time, allow the resin fiber to expand freely without bowing up or being compressed. Since the stainless steel tubes allow the lead

fibers to slide in and out during the cure monitoring process, temperature can vary over a large range (25 - 200 °C) without causing the above mentioned resin fiber bowing (see Figure 2). Furthermore, we machined the aluminum resin pool blocks such that the resin fiber will always be placed in the same fashion within the resin pool. Three different resin pool blocks with varying interaction lengths and incorporated fire rod elements have already been manufactured for future interaction length dependency tests. All resin pool blocks include a small orifice directly underneath the pool to monitor resin temperature.

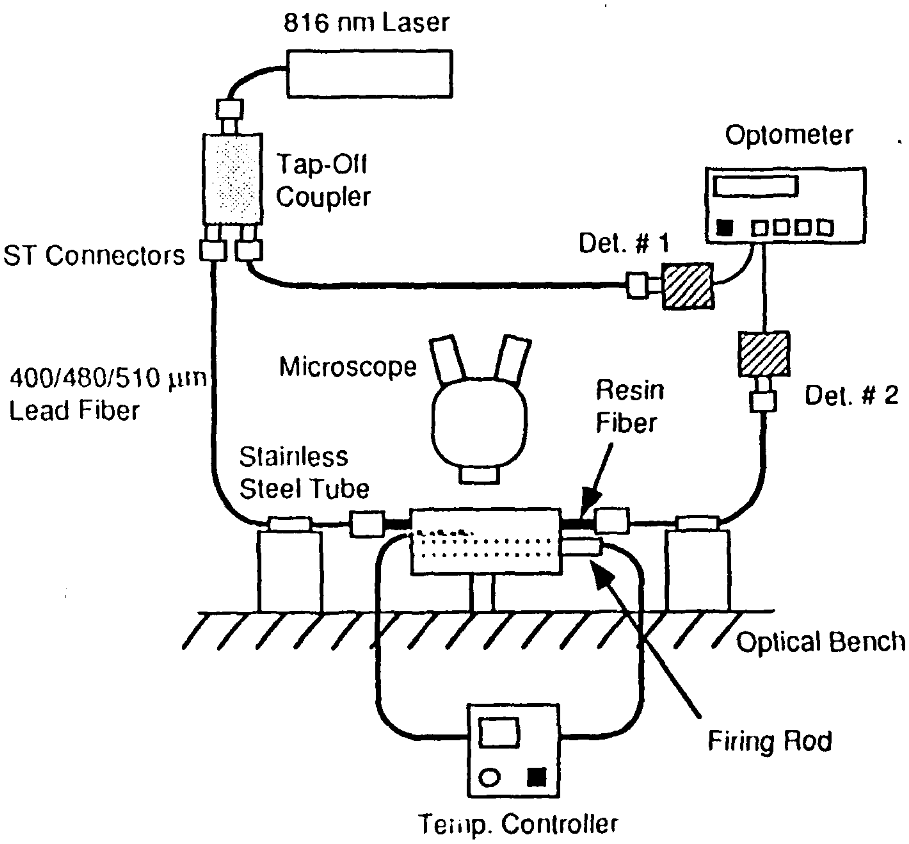

Figure 2: The Modified Epoxy Cure Monitoring Station.

3.1.4. Preliminary Hercules 3501-6 Cure Monitoring Results:

Using the set-up shown in Figure 2 we proceeded to perform the first cure monitoring experiments with the Hercules 3501-6 resin. The experiment conditions are summarized in the table shown in Figure 3. We used a 4.0 cm interaction length and constant 180 °C cure temperature. After dividing the reference power of channel 2 into the transmitted signal power of channel 1, and normalizing this ratio to its original value at t = 0 we obtained the normalized

transmitted power versus time plot shown in Figure 4. Repeatability of this plot must yet be verified.

Operating Wavelength:	816 nm
Source Type:	GALA CW Laser System, 3 mW Output
Detection Scheme:	Dual Channel, Refrenced
Detector Cal. Wavelength:	825 nm
Detector Integ. Time:	1 sec
Resin Fiber Interaction Length:	4.0 cm
Resin Temperature:	180 °C
Lead Fiber Type:	400/480/510 μm Polyimide Coated
Resin Fiber Diameter:	508 μm

Figure 3: Conditions for the Hercules 3501-6 Resin Cure Monitoring Experiment.

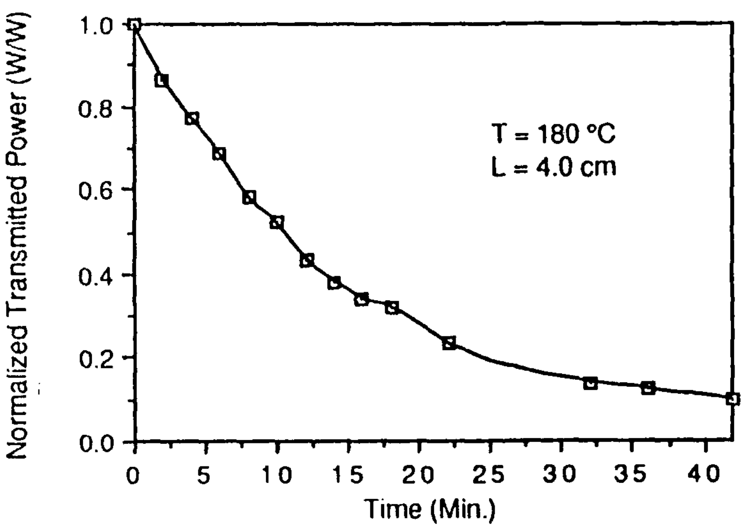

Figure 4: Preliminary Hercules 3501-6 Resin Cure Monitoring Results.

3.2. The Distributed Fiber Optic Temperature Sensor:

Until we have verified that the proposed epoxy cure monitor can be calibrated to compensate for temperature fluctuation induced refractive index changes, it is necessary to use an embedded fiber optic temperature sensor which tracks the temperature surrounding the resin fiber. Whether or not the temperature sensor performance warrants it to be permanently incorporated into the composite structure for post process sensing applications must be decided after all testing is completed. At this point we are already optimistic that, through proper cure monitor calibration, referencing, and normalization, temperature monitoring may not be required as part of routine composite cure monitoring processes. This must of course be verified and confirmed. If this is the case, the developed fiber optic distributed temperature sensor can be used for either cure

monitoring calibration purposes or as a "stand-alone" sensor to be used in a number of smart structure applications.

3.2.1. Design and Fabrication of the Distributed Fiber Optic Temperature Sensor:

The design of the temperature sensor to be used for cure monitor calibration purposes consists of a 150 μm I.D. , 370 μm O.D. polyimide coated silica hollow core fiber which is filled with a Hydrogenated Terphenyl fluid (forming the Liquid Core Fiber or LCF), and a reservoir package at each of its ends (see Figure 5). The refractive index of the fluid at room temperature is 1.528 and has a β of -3.8×10^{-4}. These properties insure it to posses a T_{crit} of approximately 180 °C, the recommended cure temperature for the Hercules 3501-6 resin. The fluid itself is introduced into the polyimide coated capillary by a suction process similar to that used for filling the resin fiber mold. In this case it is not necessary, however, to perform this process at elevated temperatures, making it relatively easy to fill fibers which are as long as 1 - 2 m. The thermal characteristics of all temperature sensor materials, including the Hydrogenated Terphenyl, are such that temperatures as high as 250 °C can be withstood.

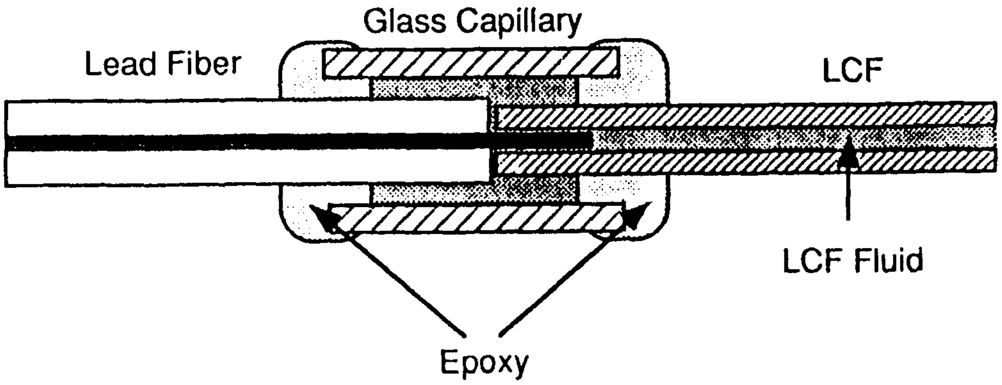

Figure 5: Lead-to-Liquid Core Fiber Interface Reservoir of the Fiber Optic Temperature Sensor.

3.2.2.Testing of the Distributed Fiber Optic Temperature Sensor:

After manufacturing a 0.61 m long temperature sensor, it was placed within a silicone fluid filled temperature chamber. The actual sensor interaction length was 0.46 m with both fluid reservoirs remaining outside of the chamber (see Figure 6). A referencing approach similar to that of the cure monitor was used to track laser output drift by tapping a portion from the input signal and sending it straight to a separate detector (channel 2). Temperature within the chamber was raised from room temperature to 190 °C using a heating tape wrapped around the chamber. As can be seen from the graph in Figure 7, normalized, referenced transmitted intensity begins to drop off sharply at approximately 170 °C and reaches a minimum at approximately 185 °C. Also evident is the

device's sensitivity in the range of interest (178 °C) showing a steep, almost linear decay in this regime. This seems to indicate that the fluid selection process (Task 2) has been accomplished successfully. In the future, it will be necessary to investigate the performance of the device for lengths which are closer to the composite structure's dimensions, probably in the 5 - 10 cm range. For such lengths the transmitted power roll-off may not be as steep but should still occur at approximately 180 °C.

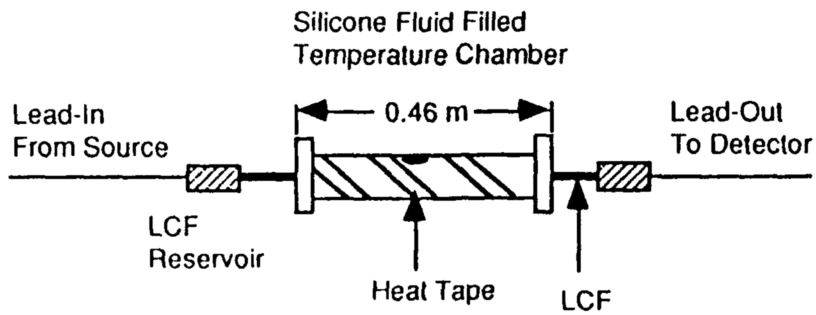

Figure 6: Fiber Optic Temperature Sensor Experiment Set-Up.

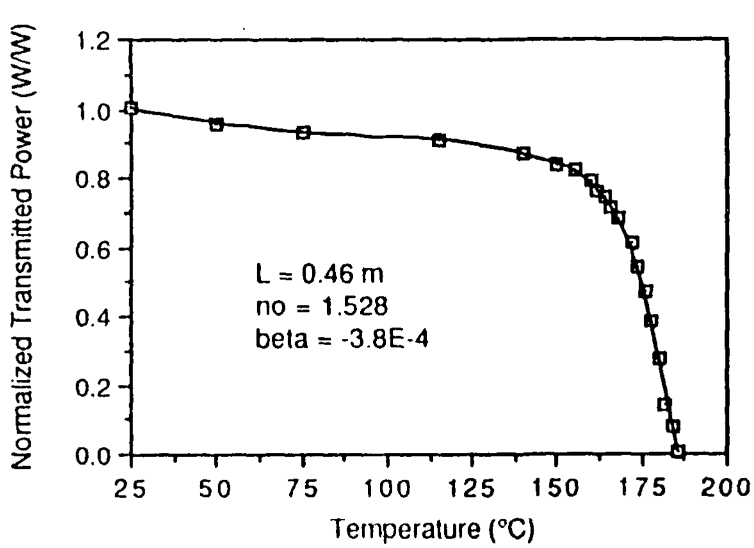

Figure 7: Fiber Optic Temperature Sensor Experiment Results.

4.) UPCOMING TASKS:

During the next month we will complete Task 1 and Task 2 by performing the remaining epoxy cure monitor experiments (improving sensitivity) and completing the development of the temperature sensor (test shorter lengths, embed sensor in resin). A major part of the third month efforts will be spent on demonstrating experiment repeatability. This includes, for example,

studying the interaction length effects of both monitors on device sensitivity. We will also begin addressing Task 3, integrating both monitors, by using a single monitoring system to acquire all data. Plans have also been made to perform hot press and autoclave experiments using facilities at Virginia Tech's Composites Fabrication Laboratory. These experiments are currently scheduled to begin during the fourth month of this contract (October 1990).

5.) CONCLUSIONS:

During the second month of SBIR Phase 1 contract # DAAL04-90-C-0013 we have accomplished the following:

- We have modified the cure monitor resin fiber fabrication process to allow us to obtain smaller diameter (508 μm), longer length (15 cm) fibers in a repeatable, high yield fashion.
- We have developed a lead-to-resin fiber package which minimizes the interface losses, eliminates relative fiber movement, and avoids the use of micropositioners.
- We have modified the cure monitoring station to apply uncured resin repeatably and uniformly for calibration purposes.
- We have performed cure monitoring experiments using the modified station.
- We have designed and fabricated a fiber optic temperature sensor for embedded composite applications.
- We have tested the temperature sensor and demonstrated its performance at the temperature range of interest (170 - 185 °C).

Upcoming tasks during the third month of this contract include finishing all cure monitor calibration experiments (repeatability), demonstrating the performance of the temperature sensor in an embedded application, and beginning to address interfacing of both devices.

6.) REFERENCES:

[1] FIMOD Corp.SBIR Phase 1 Proposal "Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials", Dec. 29, 1990, pp.8 - 14.

[2] FIMOD Corp. Monthly Technical Status Report (7/16/90 - 8/14/90) "Optical Fiber Sensors for Organic Matrix Composite Materials"

[3] B. Zimmermann et al, "A Novel Liquid Core Fiber Temperature Sensor for Smart Structure Applications", Jan. 1990 Issue of the Journal of Intelligent Material Systems and Structures.

[4] A. Hartog et al, "A Distributed Temperature Sensor Based on Liquid-Core Optical Fibers," J. of Lightw. Tech., Vol. LT-1, No. 3, pp. 498 - 509, (Sept. 1983).

APPENDIX C

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

Monthly Technical Status Report (9/11/90 - 10/12/90)

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Report Submitted to:

U.S. Army Materials Technology Laboratory
ATTN: SCLMT-MEC (PRA)
Watertown, MA 02172-0001

Contract # DAAL04-90-C-0013

Author of Report:

Bernd D. Zimmermann

Date of Report:

October 15, 1990

SUMMARY:

The following is the third monthly technical status report regarding contract DAAL04-90-C-0013 submitted to the USAMTL in Watertown, MA. The report describes the activities and progress during the third month of this project as pertaining to the submitted SBIR Phase 1 proposal ("Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials"). Progress during this period includes completing final modifications to the resin fiber fabrication process, implementing calibration testing using specially designed resin heating blocks of lengths ranging from 2.6 to 7.8 cm, and developing software to interface the cure monitor with an IBM personal computer. Calibration testing using the specially designed heating blocks has shown that, due to the resin's exothermic behavior, temporal normalization of the acquired data has to be performed to obtain repeatable results. Further testing in upcoming weeks using the developed software should demonstrate that this normalization is possible not only for neat resin cure monitoring, but also during prepreg processing. Upcoming tasks include the verification of the temporal normalization procedure, completion of the interface software, and hot press testing.

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

1.) INTRODUCTION:

The following document is aimed at reporting progress achieved on contract DAAL04-90-C-0013 during the period of 9/11/90 through 10/12/90. During this third month of the project we have achieved reasonable confidence in fabricating good quality Hercules 3501-6 resin fibers. The resin fiber fabrication techniques discussed in the second monthly report have proven to be suitable for all upcoming Phase 1 experiments. Minor modifications to this fabrication process during this month will be discussed. We have also demonstrated that the modified epoxy cure monitoring station presented in the second monthly report (see Fig. 2, p. 6) is more than adequate to perform all neat resin cure monitoring experiments, including cure monitor calibration. Standard resin pool blocks using precisely dimensioned firing rods and specific resin fiber interaction lengths have been developed, and are discussed in this report. Emphasis was placed on obtaining repeatable neat resin cure monitoring results. Such results have been obtained with the 7.8 cm interaction length set-up, after observing what are believed the effects of an exothermic reaction at the beginning of the cure process. We will discuss how the exothermic behavior of the Hercules 3501-6 resin may affect the cure monitoring results. Although the development of the embedded temperature sensor is temporarily on hold since its impact on the performance of the cure monitor has not yet been seen as significant, we have manufactured three 20 cm long sensors for use in upcoming hot-press, prepreg experiments.

2. BACKGROUND:

2.1. Fiber Fabrication:

The fabrication of the Hercules 3501-6 resin fibers for cure monitoring has shown to be adequate for all remaining Phase 1 experiments. At this point we have the capability of producing nine fibers of 12 - 15 cm length at a time using the mold fabrication process described in previous reports. Two minor modifications to this process, however, have been implemented. To avoid flow of the resin into the Sylgard 184 mold capillaries before all air bubbles in the resin have been allowed to escape, the capillaries are blocked with Kapton tape up until just prior to the suction step. Also observed was the fact that either oxidation or other chemical interaction between the hot resin and the aluminum mold casing was causing some type of off-gassing which raised the gaseous content of the resin prior and during succtioning. To avoid the effects of these reactions, Kapton tape was also used to prevent the resin from getting in contact with the aluminum casing. In this manner the resin would only be in direct contact with the Kapton tape and Sylgard mold, both of which do not react with the resin.

2.2. Cure Monitor Assembly:

The assembly of the resin cure monitor presented in the last monthly report has proven itself to work very well. Although we have noticed that the adhesion between the UV elastomer and resin fiber after the elastomer has been allowed to cure is not as strong as that between the elastomer and glass capillary and/or lead fibers (see Fig. 1, p. 5 of 2nd monthly report), it suffices for all subsequent Phase 1 experiments. In the future other adhesive materials may be evaluated for ultimate assembly ruggedization. Also observed was the fact that the UV elastomer does not withstand temperatures above ~125 °C, which at this point is not a problem since the assembly packages are not being exposed to such high temperatures.

2.3. The Embedded Temperature Sensor:

As stated in the introductory section, the work on the embedded temperature sensor is temporarily on hold to allow us to focus on obtaining repeatable cure monitor results. Although efforts are being shifted to concentrate on the development of the cure monitor, we have already manufactured three 20 cm long liquid core fiber temperature sensors with a switching temperature of approximately 175 °C (see Fig. 7, p. 9 of the 2nd monthly report). These sensors will be utilized in upcoming hot-press, Hercules 3501-6 prepreg cure monitoring experiments scheduled for the latter part of October 1990. As was discussed in the 2nd report, the fluid was chosen to posses thermo-optic properties to result in a switching temperature which coincides with the resin's recommended cure temperature. The sensor itself has been shown to work properly, however, improvements in performance are anticipated after evacuating the fluid before incorporating it into the hollow core silica fiber. This should avoid air pockets which may be created in the liquid core fiber when temperature is decreased abruptly. The forming of such air pockets has been observed on occasion right at the lead-to-liquid core fiber interface after thermally shocking the sensor.

3.) EXPERIMENTS:

3.1. Cure Monitor Calibration/Repeatability Experiments:

Although the basic principle of operation (i.e., the decrease of the transmitted optical signal intensity as a function of cure time) of the cure monitor was demonstrated during the first two months of this project, it remained to be shown that repeatable transmitted intensity versus cure time behavior could be obtained. Towards achieving this objective, first with neat resin specimens, we built specific resin heating blocks of varying fiber interaction lengths to be used as part of the cure monitoring station discussed in previous reports. The heating blocks were machined out of aluminum with interaction lengths of 2.6, 5.2, and 7.8 cm. The design of the

block to be used for calibration purposes is shown in Figure 1. Notice that the length of the firing rods used equal the length of the block to a) avoid heating up the assembly packages, and b) simulate a hot-press environment. A thermocouple is placed right above the firing rod, underneath the resin pool, and 0.7 mm holes are drilled at either end of the pool to run the resin fiber through. Kapton tape is used again at the bottom and sides of the pool to avoid resin/aluminum interaction. The block is easily cleaned after the cure monitoring process is completed by running a drill bit through the length of the pool on a lathe.

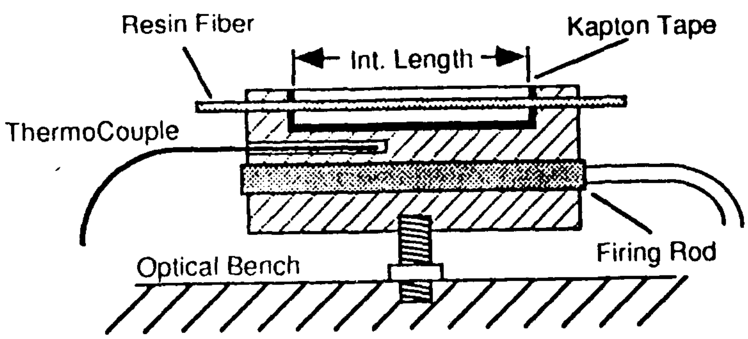

Figure 1: Heating Block Assembly for Neat Resin Cure Monitor Calibration Experiments.

Using the above resin heating blocks we performed cure monitoring using the three interaction lengths mentioned above. The test conditions are very similar to those listed in Fig. 3, p. 7 of the 2nd monthly report, except now the interaction length would vary (see Figure 2). Referring to Fig. 4, p. 7 of the last report, it was stated that an exponential decay in normalized transmitted power as a function of time could be observed. Further experimentation using 5.2 cm interaction length fibers shows that the decay in normalized transmitted power may not be exponential, but rather Gaussian (see Figure 3). An explanation for the discrepancy in the shapes of these decaying curves is that in the experiments reported last time a preheating cycle at 124 °C was used for approximately 10 minutes to cause any remaining air pockets in the resin to escape. During this time the resin was already being exposed to elevated temperatures which probably initiated the gelling process. Time, t = 0 was chosen after the 10 minutes, at which point the temperature was raised to 180 °C. Now, instead of preheating the resin, temperature is initially set at 180°C, the resin is immediately dropped into the heating blocks straight from the freezer and t = 0 is chosen at the time the resin has molten enough to completely surround the cured resin fiber.

Operating Wavelength:	816 nm
Source Type:	GALA CW Laser System, 3 mW Output
Detection Scheme:	Dual Channel, Refrenced
Detector Cal. Wavelength:	825 nm
Detector Integ. Time:	1 sec
Resin Fiber Interaction Length:	2.6, 5.2, 7.8 cm
Resin Temperature:	180 °C
Lead Fiber Type:	400/480/510 μm Polyimide Coated
Resin Fiber Diameter:	508 μm

Figure 2: Conditions for the Hercules 3501-6 Cure Monitoring Experiments.

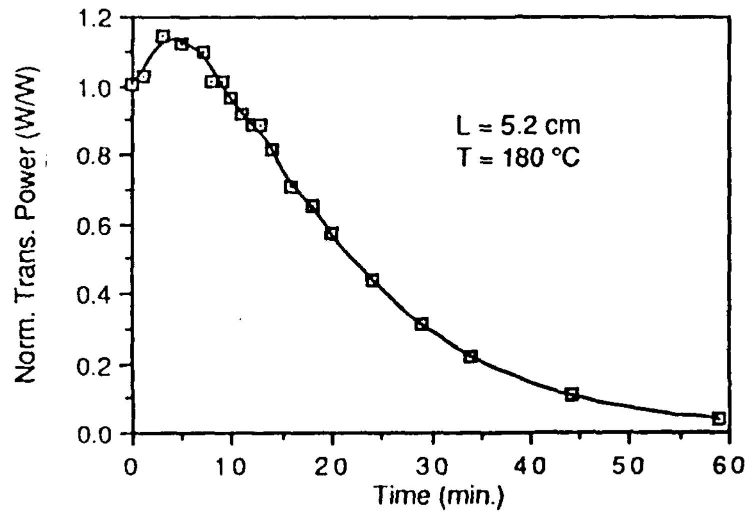

Figure 3: Hercules 3501-6 Cure Monitoring Results Without Preheating Conditions.

A number of experiments were also conducted using a 7.8 cm interaction length. Three trials were conducted with results as shown in Figure 4. Notice that in all trials an increase in normalized transmitted power is seen at the beginning of the cure process, after which the Gaussian decay occurs. From the graph in Figure 4 one might first be of the opinion that the results are not very repeatable, especially considering that the test conditions among all three trials were identical. The initial increase in transmitted power, however, is an indication that exothermic reactions might cause the resin to heat up beyond 180 °C, which is not immediately picked up by the thermocouple which is placed underneath the resin pool. Increased transmitted power due to increased temperature is typical of these resin fibers due to what is believed to be a decrease in material density. Such behavior is always seen when the fiber is brought from room temperature to 180 °C. Assuming that the effects of what is currently expected to be exothermic reactions are highly unpredictable, and probably depend strongly on a number of different processing parameters including the volume of material to be cured, we proceeded to set t = 0 at the point in

time at which the transmitted power had reached a maximum (we will refer to this procedure as "temporal normalization"). This maximum usually occurred within 3-4 minutes after the resin was placed in the heating block. Once the transmitted power values were normalized to that point in time (see Figure 5), a repeatable trend seemed to exist. It remains to be verified that this repeatability can also be obtained for other interaction lengths, especially since the effects of the exothermic reactions are much less significant for lower volumes of resin material. Identifying the transmitted power peak for smaller amounts of material might be difficult.

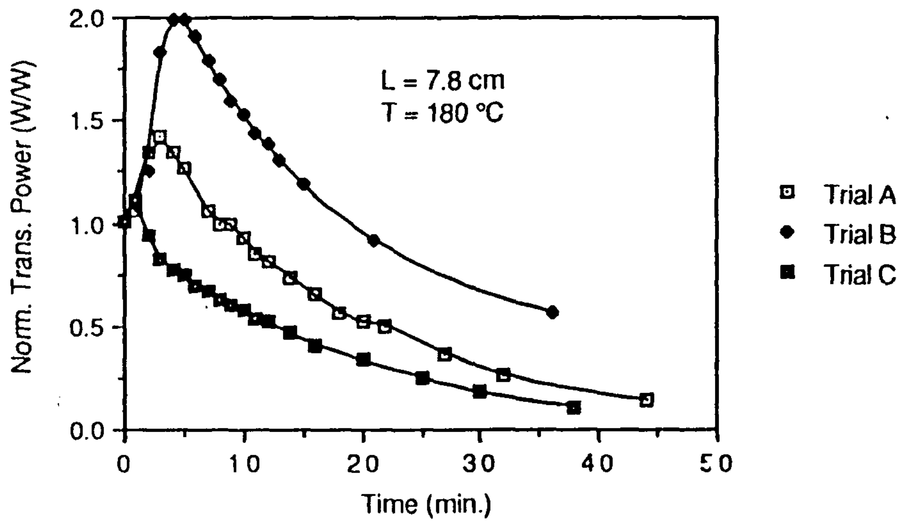

Figure 4: Cure Monitoring Results for a 7.8 cm Resin Fiber Before Temporal Normalization.

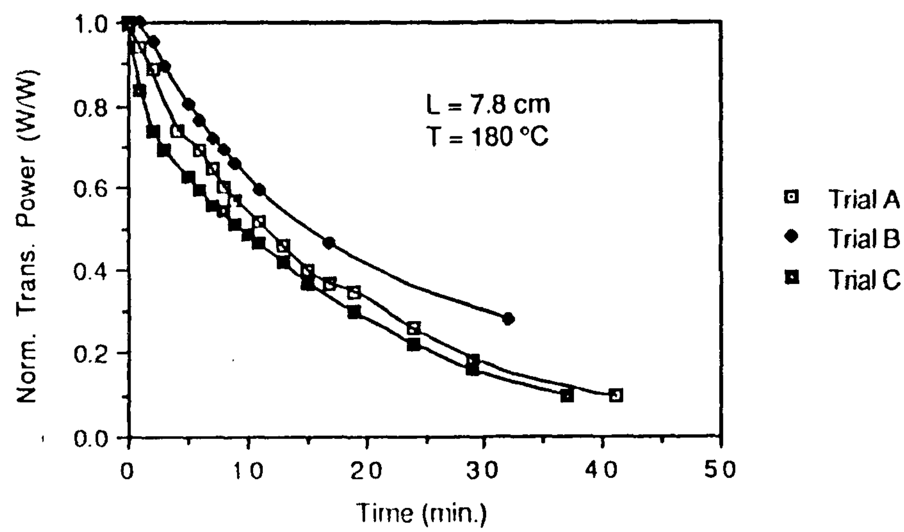

Figure 5: Cure Monitoring Results for a 7.8 cm Resin Fiber After Temporal Normalization.

3.2. PC Interfacing/Data Acquisition:

From the above it is obvious that automatization of the cure monitoring process is not only highly convenient but almost inevitable. Up to this point data has been taken manually only every minute. In anticipation of a need to perform numerous calibration experiments not only on the neat resin, but also for future hot-press experiments, we have started developing software written in PC Basic to interface the UDT S390 Optometer with an IBM personal computer. A preliminary version of the program which performs the interface functions allows the user to select the time interval between measurements, pick the number of detector channels to be monitored, and store the measured data in an ASCI file on the computer hard disk. In the future the software can be adapted to include data acquisition from other embedded sensors, including the temperature sensor.

4.) UPCOMING TASKS:

Tasks to be addressed during the fourth month of this contract include completion of the software to interface the cure monitor with an IBM PC, designing and implementing modifications to a Carver hot press to allow prepreg cure monitoring, and acquiring bulk raw material (both neat resin and prepreg) for intensive testing during the last two months of the Phase 1 effort. The software to interface the cure monitor to the computer is almost completed. An IBM personal computer has been set up next to the cure monitoring station and the Carver hot press with a GPIB bus connected to the UDT S390 Optometer. Preliminary testing of this program is scheduled for next week. Modifications to the Carver hot press consist mainly of reducing the plate size from approximately 6" x 6" to 2" x 6". This will allow us to manufacture coupons with embedded resin fibers without compressing the lead fiber packages and/or exposing them to elevated temperatures. Raw material currently to be shipped includes Hercules 3501-6 neat resin and prepreg sheets. The resin is scheduled to arrive this week.

5.) CONCLUSIONS:

During the third month of SBIR Phase 1 contract # DAAL04-90-C-0013 we have accomplished the following:

- We have completed final modifications to the Hercules 3501-6 resin fiber fabrication process allowing us to repeatably manufacture 508 μm diameter fibers 12 to 15 cm in length.
- We have designed, built, and tested resin heating blocks for calibration purposes. The block interaction lengths range from 2.6 to 7.8 cm, and allow repeatable application of the uncured resin over the resin fiber.

- We have used the heating blocks to identify the effects of the exothermic behavior of the resin during the cure process. Temporal normalization of the obtained normalized transmitted power versus time curves seems to compensate for the uncertainty of these effects.

- We have begun with the development of software which will allow us to interface the cure monitor with an IBM personal computer. A GPIB bus has already been installed, linking the UDT S390 Optometer with the PC.

Upcoming tasks during the third month of this contract include verification of the temporal normalization procedure, completion of the interface software, and hot press testing to perform cure monitoring on prepreg composite specimens.

6.) REFERENCES:

[1] FIMOD Corp.SBIR Phase 1 Proposal "Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials", Dec. 29, 1990, pp.8 - 14.

[2] FIMOD Corp. Monthly Technical Status Report (7/16/90 - 8/14/90) "Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring".

[3] FIMOD Corp. Monthly Technical Status Report (8/15/90 - 9/10/90) "Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring".

APPENDIX D

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

Monthly Technical Status Report (10/13/90 - 11/9/90)

Prepared by:

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Report Submitted to:

U.S. Army Materials Technology Laboratory
ATTN: SCLMT-MEC (PRA)
Watertown, MA 02172-0001

Contract # DAAL04-90-C-0013

Author of Report:

Bernd D. Zimmermann
Bernd D. Zimmermann

Date of Report:

November 17, 1990

SUMMARY:

The following is the fourth monthly technical status report regarding contract DAAL04-90-C-0013 submitted to the USAMTL in Watertown, MA. The report describes the activities and progress during the fourth month of this project as pertaining to the submitted SBIR Phase 1 proposal ("Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials"). Accomplishments during this month include the development of a method to determine the rate of cure of the Hercules 3501-6 resin by performing a numerical integration of sensor transmitted power as a function of time, completion of the PC interface software, modifications to a Carver hot press for fabrication of Hercules AS4/3501-6 prepreg based coupons, and preliminary testing of the hot press set-up. Tasks for next month include performing further experiments with the recently established coupon fabrication process, conducting the cure monitoring process using a real time determination of cure rate, and establishing a cure criterion based upon cure rate.

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

1.) INTRODUCTION:

The following document is aimed at reporting progress achieved on contract DAAL04-90-C-0013 during the period of 10/13/90 through 11/9/90. During this fourth month we have addressed the need for data normalization and subsequent data interpretation, the development of software to retrieve information from a multiple channel optometer and single channel temperature probe, the modifications necessary to perform cure monitoring using a Carver hot press, and preliminary tests using Hercules AS4/3501-6 prepreg. In last month's report it was stated that temporal normalization of the transmitted intensity versus time curves was required for repeatability. It is speculated that handling of the composite material, either neat resin or prepreg, immediately after removal from the freezer impacts the way the material behaves early during the cure process. The impact of pre-cure material exposure to room temperature will be discussed in this report. Furthermore, it will be required to establish a state-of-cure criterion which determines whether a sample passes certain cure characteristics. Toward this objective we will present a technique which uses the rate of transmitted power change to identify state of cure. It is hoped that the data normalization in conjunction with the real time numerical differentiation will yield a reliable state-of-cure criterion.

2.) BACKGROUND:

In last month's status report it was stated that temporal normalization of the transmitted power versus time was necessary to obtain repeatability in the cure monitoring experiments. The temporal normalization was achieved by using the point in time at which maximum normalized transmitted power was attained as $t = 0$, the beginning of the cure cycle. Three trials using a 7.8 cm resin fiber interaction length were conducted at a constant resin temperature of 180 °C. The three trials yielded different transmitted power versus cure time curves, indicating that slight differences in handling of the neat resin samples may have caused some samples to reach a peak transmitted intensity sooner than others. It was shown that by using $t=0$ at the maximum transmitted power, and normalizing the data to this point, reasonable repeatability was obtained (see Fig. 5 of last month's report). The transmitted power peaking behavior was attributed to exothermic chemical reactions occurring just prior to resin gelling. This phenomenon is well known to exist with many of today's composite resins, and its impact is dependent on a number of processing parameters and conditions (cure temperature, amount of resin, mold type, etc.). For the 7.8 cm interaction length neat resin experiments, the temporal data normalization did in fact eliminate the uncertainty due to this effect.

The next task was to establish a method by which it would be possible to determine a criterion representative of the state of cure. It was also necessary to consider more typical resin cure parameters which included a preheat cycle to condition the resin prior to initiating the gel process.

3.) EXPERIMENTS:

3.1) Data Acquisition:

As stated in last month's report, efforts had been made to begin development of the software necessary to interface the UDT S-390 Optometer with an IBM PC through a GPIB data bus. In addition to allowing permanent storage of all four channel outputs of the S-390 as a function of cure time, the program should also be capable of recording cure sample temperature. After completing the first software requirement, an analog output from the Omega thermocouple used in previous experiments was fed into a Data Translation 2814 A/D board. The 0 - 1 V analog signal is tapped from the Omega LED display with a unity gain amplifier circuit preventing excessive current draining from the display. The A/D board is accessed through code included in the original software written in PC basic.Calibration was verified from room temperature to 200 °C. A listing of the program is given in Appendix A for reference. In its present format, the program displays and stores the measurement interval (minimum interval time is approximately 5 sec.), the four S-390 channel output intensities (only two of which are currently used: one is the cure monitor signal, the other one is the cure monitor reference), and the calibrated temperature values. All values can be stored either on the PC hard disk or a 5.25 " floppy disk in ASCI format.The routines used to plot the data can be chosen according to preference by the user. We opted to transfer the data into a Macintosh plotting routine called Cricket Graph. Finally, modifications to the program listed in Appendix A can easily be incorporated in the future to allow real time computation and display of resin rate of cure.

3.2) Determination of the Resin Rate of Cure:

Although temporal normalization of the obtained data allows identification of the beginning of the cure cycle, a criterion is required to establish state of cure well into the cure process. Thus, it is logical to use the rate of decay of the normalized transmitted power as a measure of cure. The rate of cure can be obtained by numerically differentiating the normalized transmitted power values as a function of time (or measurement interval). This was performed using the data obtained from three trials using a 2.6 cm interaction length resin fiber exposed to 100 °C preheat for approximately 6 minutes, and 170 °C subsequent cure temperature for a total of 400 measurement intervals (12.67 sec. each), or approximately 85 minutes. The transmitted power-versus-interval curves are plotted in Figure 1. As in previous experiments, a variability in behavior

is observed among the trials due to what is beleived to be the result of different pre-cure resin handling. Nonetheless, it was possible to numerically differentiate the data to obtain rate-of-cure curves. To minimize the noise and cause the $d(P_{sig}/P_{ref})/dt$-versus-interval curves to be smoother, it was chosen to use only the data points of every tenth measurement of the 400 taken, resulting in three sets of 40 rate-of-cure data points (see Figure 2). In all three trials, the rate of cure approaches 0.00 as the sample reaches its fully cured state. At this point it is still unknown why the first trial (Trial A) yielded a much smoother curve than trials B and C. The average of the three trials is shown in Figure 3, were it can be seen how $d(P_{sig}/P_{ref})/dt$ approaches 0.00 as the neat resin sample cures. After further testing, it should be possible to determine an absolute $d(P_{sig}/P_{ref})/dt$ for each interaction length at given processing conditions which will insure an acceptable level of cure. Obviously, this level will have to be larger in magnitude than the maximum noise level which may be encountered in any of the experiments. Currently, this noise level is still relatively high. However, if the conditions of Trial A can be repeatably achieved, the absolute $d(P_{sig}/P_{ref})/dt$ level may be as low as 1.26/sec.

At the time the above experiments were conducted the temperature monitoring option had not yet been included in the software. Future experiments will include the temperature profile superimposed on the same graph. Also for consideration in the future are modifications to the existing software which will perform the numerical differentiation in real time as the monitoring process is in progress. As stated earlier, these modifications can easily be incorporated into the existing program listed in Appendix A..

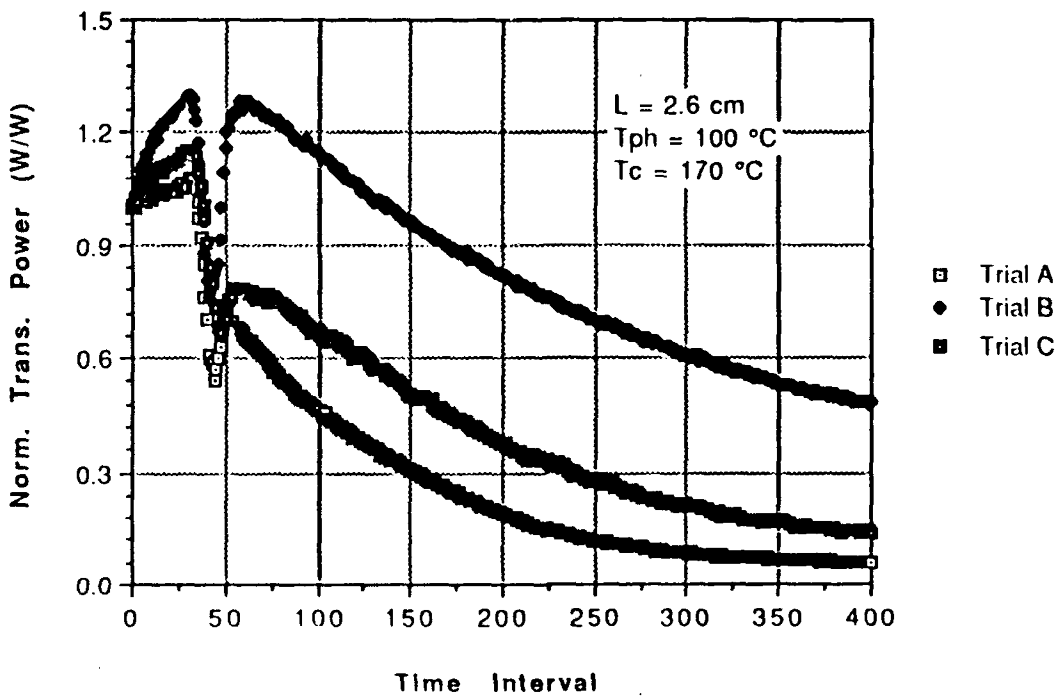

Figure 1: Hercules 3501-6 Resin Cure Monitoring Results Before Numerical Integration.

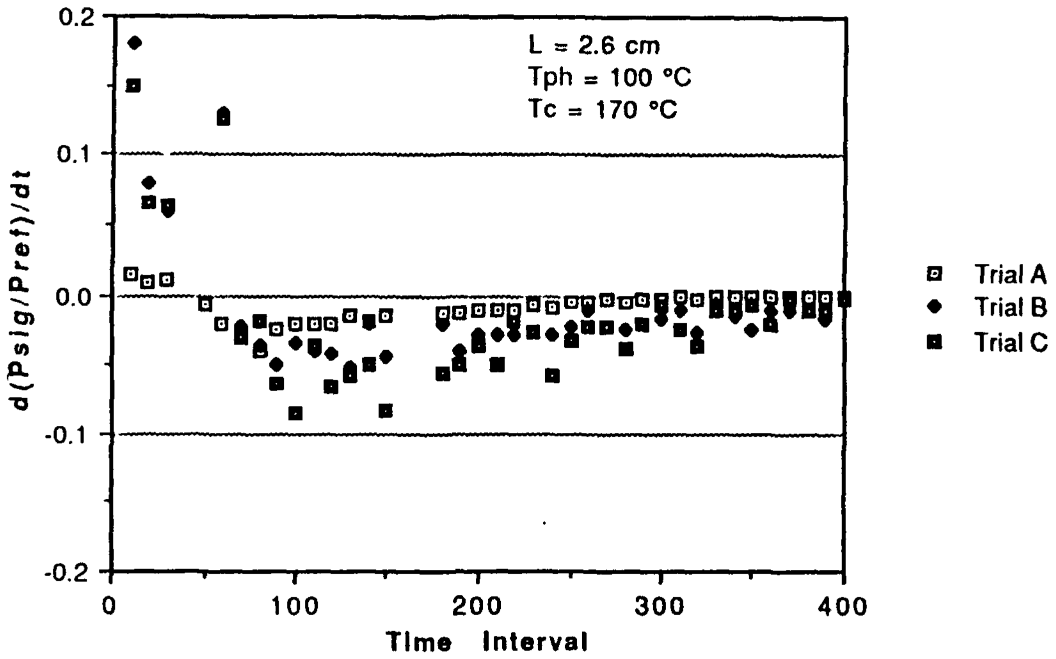

Figure 2: Hercules 3501-6 Resin Rate of Cure as a Function of Measurement Interval.

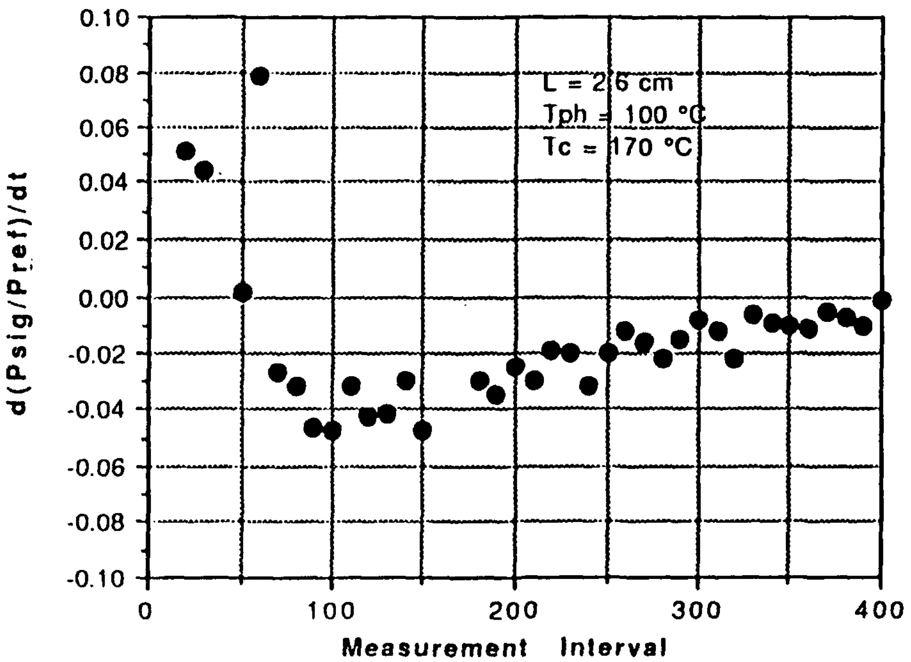

Figure 3: Average Hercules 3501-6 Resin Rate of Cure as a Function of Measurement Interval.

3.3) Hot Press Modifications:

In anticipation of more realistic cure monitoring experiments using Hercules AS4/3501-6 prepreg samples, we have completed all modifications on a 15 x 15 cm Carver, hot press necessary for composite coupon manufacturing. The press was modified such that 4.5 x 15.0 x 0.5 cm coupons could be fabricated. An aluminum mold with these dimensions was machined to allow placement of the monitoring resin fiber across the coupon at a height of approximately 0.25 cm. A crossection of the set-up is shown in Figure 4. Notice how the original 15 x 15 cm plates have been partially insulated with fiberglass tape to avoid excessive heat exposure of the lead fiber packages. The mold was coated with a release agent to allow removal of the coupons after completion of the cure process for future coupon tensile testing. Teflon release sheets were also used on the top and bottom of the coupon to ease the coupon retrieval process.

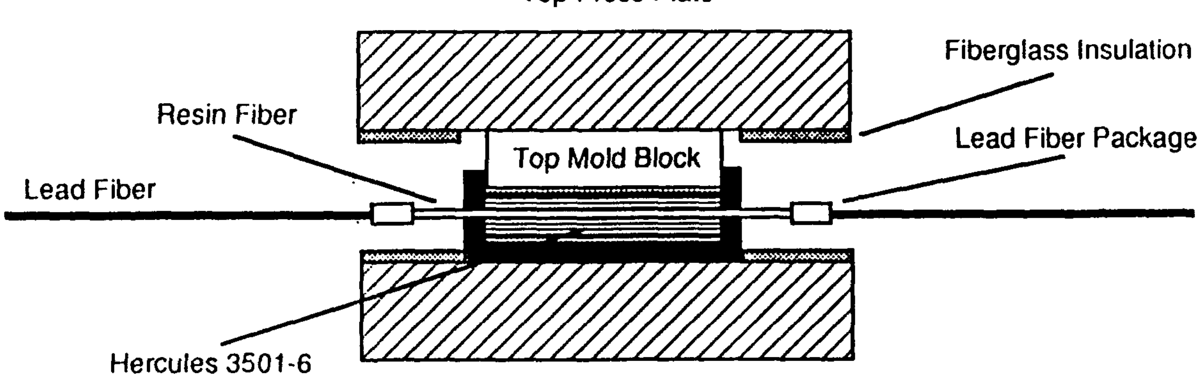

Figure 4: Hot Press Cure Monitoring Set-Up Using Fiber Optic Cure Monitor.

3.3 Preliminary Hercules AS4/3501-6 Prepreg Experiments:

The preliminary tests using the Hercules AS4/3501-6 prepreg material consisted of first testing out the mold without any resin fibers within the coupon to check the coupon fabrication process. A total of 32 plies were layed up in a 0-90-0 ° orientation to result in a total coupon thickness of approximately 0.5 cm after curing. Minimal flow of resin material was observed through the resin fiber access ports during the cure process. Next, a 7 cm resin fiber was run through the resin fiber access ports across the coupon on top of the 16th ply. However, the resin fiber was not yet used to monitor cure. The coupon was processed in the same fashion as in the first trial, and after post cure inspection, seemed to have blended in with the coupon material. Some leakage of resin material was observed around the top mold block when applying pressure. Some of this leakage may be minimized in the future by sealing the top mold block to the mold itself with polyimide tape.

This should allow application of the recommended 85 psi of pressure during cure without experiencing resin leakage. Immediately following these preliminary tests, trials will be conducted in the next few weeks with resin fibers which will actively be monitored.

4.) UPCOMING TASKS:

As the fifth month of the Phase I project approaches, it will be the objective to pull together all of the information and data obtained to date to determine how the neat resin experiments will correlate with the prepreg coupon tests. The actual testing of the coupon cure monitoring is scheduled for the beginning of December, 1990. This testing will include the aforementioned software modifications which will allow real time display of cure rate. All necessary raw materials including prepreg, resin, and lead fibers for at least the duration of Phase I, and part of Phase II are available. The experimental part of this contract is expected to be completed by the end of December 1990, after which a draft of the Final Project Report will be pieced together. Two copies of this draft (1 to PRA , 1 to MEC) will be delivered by February 3, 1991 as agreed upon in contract DAAL04-90-C-0013. Suggestions on what we believe would be a very successful continuation of this Phase I work will be made within the Final Project Report. Twelve copies of the revised Final Report will be delivered by March 3, 1991 to conclude this Phase I program.

5.) CONCLUSIONS:

During the fourth month of SBIR Phase I contract # DAAL04-90-C-0013 we have accomplished the following:

- We have developed a method to determine the rate of cure of the Hercules 3501-6 composite material by numerically differentiating the transmitted power as a function of time. Three trials were conducted using neat resin to demonstrate how the decay rate of transmitted power through the resin fiber approaches zero as the material reaches its fully cured state.

- The software to interface the UDT S-390 Optometer and an Omega Thermocouple with an IBM personal computer through a GPIB data bus and a Data Translation 2814 A/D board has been completed. Experimental runs using this software have already been performed successfully.

- Modifications to a Carver hot press have been implemented to allow fabrication of Hercules AS4/3501-6 prepreg coupons. An aluminum mold with resin fiber access ports has been machined toward this objective.

- Preliminary hot press tests with the Hercules AS4/3501-6 prepreg have been conducted. The coupon fabrication process has been established using 32 prepreg plies in a 0-90-0 ° orientation lay up.

Upcoming tasks include cure monitoring experiments using the established coupon fabrication process, implementing necessary software modifications for real time determination of cure rate, and establishing an absolute cure criterion based upon cure rate.

6.) REFERENCES:

[1] FIMOD Corp.SBIR Phase 1 Proposal "Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials", Dec. 29, 1990, pp. 8 - 14.

[2] FIMOD Corp. Monthly Technical Status Report (7/16/90 - 8/14/90) "Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring".

[3] FIMOD Corp. Monthly Technical Status Report (8/15/90 - 9/10/90) "Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring".

[4] FIMOD Corp. Monthly Technical Status Report (9/11/90 - 10/12/90) "Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring".

```
1   CLEAR ,60000! : IBINIT1=60000! : IBINIT2=IBINIT1+3 : BLOAD "bib.m",IBINIT1
2   CALL IBINIT1(IBFIND,IBTRG,IBCLR,IBPCT,IBSIC,IBLOC,IBPPC,IBBNA,IBONL,IBRSC,IB
SRE,IBRSV,IBPAD,IBSAD,IBIST,IBDMA,IBEOS,IBTMO,IBEOT,IBRDF,IBWRTF,IBTRAP,IBDEV,IB
LN)
3   CALL IBINIT2(IBGTS,IBCAC,IBWAIT,IBPOKE,IBWRT,IBWRTA,IBCMD,IBCMDA,IBRD,IBRDA,
IBSTOP,IBRPP,IBRSP,IBDIAG,IBXTRC,IBRDI,IBWRTI,IBRDIA,IBWRTIA,IBSTA%,IBERR%,IBCNT
%)
5   '
6   '
10 'This program retrieves up to four outputs from the UDT S390 Optometer
20 'through a GPIB PC interface card.  The program also allows interface with a
30 'Data Translation A/D board to retrieve temperature values from an analog
35 'output thermocouple.
40 'This program was written on October 17, 1990, revised on November 10, 1990.
50 '
60 'initialization
70 B$=CHR$(9)
80 T$ = CHR$(10)     'terminating character
90 '
170 '
210 CLS
220 'Establishment of device numbers
230 UDT$ = "DEV4"                               'detector
240 CALL IBFIND(UDT$,UDT%)
250 IF UDT% < 0 THEN GOSUB 1090        'error trap if detector isn't there
290 BD$ = "GPIB0"                             'GPIB card
300 CALL IBFIND (BD$,BD%)
305 IF BD% < 0 THEN GOSUB 1120    'error trap if GPIB card is not functioning
320 'V%=0:CALL IBDMA(BD%,V%)
330 'V%=11:CALL IBTMO(DEV1%,V%)
350 REM
360 CALL IBCLR(UDT%)          'execute a device clear on the detector
371 CLS
372 INPUT"Please enter time interval (in seconds) between each reading";I
373 PRINT""
374 PRINT""
375 PRINT"Please enter the name you want for the data file containing the "
380 INPUT"information gathered in this run";FILE$
385 OPEN FILE$ FOR OUTPUT AS #1
387 PRINT " "
388 PRINT " "
390 PRINT #1," "
391 PRINT #1," Time interval between measurements = ";I;" seconds."
393 PRINT #1," "
394 PRINT #1," "
399 PRINT #1, "Interval      Chan1     Chan2      Chan3       Chan4      TEMP"
400 PRINT #1," "
420 INPUT"Hit return when ready to begin the test";R
421 PRINT " "
425 PRINT " "
426 PRINT "To terminate program hit the Control-Break keys!!!"
427 PRINT ""
428 PRINT ""
430 PRINT "Interval      Chan1      Chan2        Chan3        Chan4        TEMP"
435 PRINT " "
440 '
445 ' Take initial readings for time zero
    '
```

```
470 GOSUB 650
475 M% = M% + 1
480 '
490 '
500 TIME$="00:00:01"                                'resets the interval
510 T = TIMER
530 '
540 'Check to see if time interval has elapsed
550 IF (T/I < INT(T/I) +.1/I) AND (T/I > INT(T/I) -.1/I) THEN 470
560 GOTO 510                          'hasn't been a minute since the last reading
570 '
620 END
622 '
630 ' Subroutine to read outputs from the detector
640 '
650 OUT1$ = "G"+T$  'tells detector to begin measuring
660 CALL IBWRT(UDT%,OUT1$)
710 INPUT1$ = SPACE$(25)      'clear buffer
730 '
790 '
820 OUT4$ = "HF1"+D$
830 CALL IBWRT(UDT%,OUT4$)  'channel one to the buffer
840 INPUT3$ = SPACE$(25)        'reads the value in the buffer
850 CALL IBRD(UDT%,INPUT3$)
860 '
870 DET1 = VAL(INPUT3$)
880 'PRINT"ans(F1) = ",DET1,"answer$ = ",INPUT3$
890 OUT5$ = "F2"+ T$  'tells the detector to output the reading from
900 CALL IBWRT(UDT%,OUT5$)  'channel two to the buffer
905 INPUT4$ = SPACE$(25)        'reads the value in the buffer
910 CALL IBRD(UDT%,INPUT4$)  'reads the value from the buffer
920 '
930 DET2 = VAL(INPUT4$)
935 HOLD(5) = ANS                         'channel 2
940 'PRINT"ans(F2) = ",DET2,"answer$ = ",INPUT4$
950 OUT6$ = "F3" + T$        'tells the detector to output the reading from
960 CALL IBWRT(UDT%,OUT6$) 'channel three to the buffer
970 INPUT5$ = SPACE$(25)        'reads the value in the buffer
980 CALL IBRD(UDT%,INPUT5$)
990 '
1000 DET3 = VAL(INPUT5$)
1010 'PRINT"ans(F3) = ",DET3,"answer$ = ",INPUT5$
1020 OUT7$ = "F4" + T$          'tells the detector to output the reading from
1030 CALL IBWRT(UDT%,OUT7$)  'channel four to the buffer
1035 INPUT6$ = SPACE$(25)        'reads the value in the buffer
1040 CALL IBRD(UDT%,INPUT6$)  'reads the value from the buffer
1041 SUM=0
1042 FOR X=1 TO 10
1043 OUT &H220,0
1044 A=0
1045 A=INP(&H220)
1046 IF A>127 THEN 1047 ELSE 1045
1047 B=INP(&H221)
1048 C=INP(&H221)
1049 N=16*B+C/16
1050 N=10*N/4096-5
1051 SUM=SUM+N
1052 NEXT X
1053 TEMP=SUM*(-100)/1.3
1060 DET4 = VAL(INPUT6$)
1065 CALL IBWRT(UDT%,OUT1$)
1070 'PRINT"ans(F4) = ",DET4,"answer$ = ",INPUT6$
1071 'PRINT "  ";M%;"      ";DET1;"  ";DET2;"  ";DET3;"  ";DET4;"  ";TEMP
1075 PRINT M%;B$;DET1;B$;DET2;B$;DET3;B$;DET4;B$;TEMP
```

```
1090 PRINT"can't find the detector"
1100 GOTO 1200
1120 PRINT"can't find the GPIB card"
1130 GOTO 1200
1200 END
```

APPENDIX E

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

Monthly Technical Status Report (11/10/90 - 12/10/90)

Prepared by:

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Report Submitted to:

U.S. Army Materials Technology Laboratory
ATTN: SCLMT-MEC (PRA)
Watertown, MA 02172-0001

Contract # DAAL04-90-C-0013

Author of Report:

Bernd D. Zimmermann

Date of Report:

December 22, 1990

SUMMARY:

The following is the fifth monthly technical status report regarding contract DAAL04-90-C-0013 submitted to the USAMTL in Watertown, MA. The report describes the activities and progress during the fifth month of this project as pertaining to the submitted SBIR Phase 1 proposal ("Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials"). During this month we have completed the first successful real time, in-situ cure monitoring process with Hercules 3501-6 AS4 composite prepreg material. A 32 ply, 0-90-0° orientation coupon with dimensions of 4.5 x 15.0 x 0.5 cm was fabricated with a 508 μm diameter resin fiber embedded parallel to the graphite fibers of the 12th ply from the bottom. Results show that the behavior of the cure monitor within the composite is similar to that seen with neat resin samples. Numerical differentiation of the Normalized Transmitted Power (NTP) again seems to yield the best criterion for determining the state of cure. Preliminary suggestions are given for follow-up, Phase II funding.

Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring

1.) INTRODUCTION:

The following document is aimed at reporting progress achieved on contract DAAL04-90-C-0013 during the period of 11/10/90 through 12/10/90. During this fifth month we have performed the first real time, in-situ cure monitoring experiment using Hercules 3501-6 AS4 graphite epoxy prepreg. A 4.5 x 15.0 x 0.5 cm coupon was prepared using 32 prepreg plies layd up in a 0-90-0° orientation. A 508 μm diameter, 8.5 cm long resin fiber was embedded within the coupon to monitor resin cure. The data acquisition hardware and software developed during the previous month was implemented to yield the results presented in this report. Preliminary microscopic inspection results of the finished specimen are discussed in Section 3.3.

2.) BACKGROUND:

Last month's development resulted in a reliable experimental set-up to fabricate 4.5 x 15.0 x 0.5 cm composite coupons. Also completed was software which allowed data transfer from the UDT S390 optometer and Omega thermocouple to an IBM personal computer. The composite specimens were prepared using 32 Hercules 3501-6 AS4 prepreg plies. The fabrication experiments showed that the processes used would be compatible with the proposed fiber optic cure monitoring technique. Active cure monitoring, however, had only been verified in neat resin experiments, and had yet to be demonstrated with the coupon fabrication process.

3.) EXPERIMENTS:

3.1) Hot Press Cure Monitoring Set-up:

The set-up used for the real time, in-situ cure monitoring process was described in last month's progress report. Figure 1 below shows a crossection of the press assembly which includes the composite coupon mold. 32 plies with dimensions of 4.5 x 15.0 cm were placed within the mold in a 0-90-0° orientation with the resin fiber running parallel to the graphite fibers of the 12th ply from the bottom. The 8.5 cm long, 508 μm diameter resin fiber was accessed with standard 400/480/510 μm lead fibers through previously described lead fiber packages. A reference signal was used again to compensate for the drift of the 816 nm laser. Pressure applied with the top mold block was minimum to reduce resin leakage through the mold access ports and other crevices. Fiberglass insulation tape was used again to protect the lead fiber packages from excessive heat.

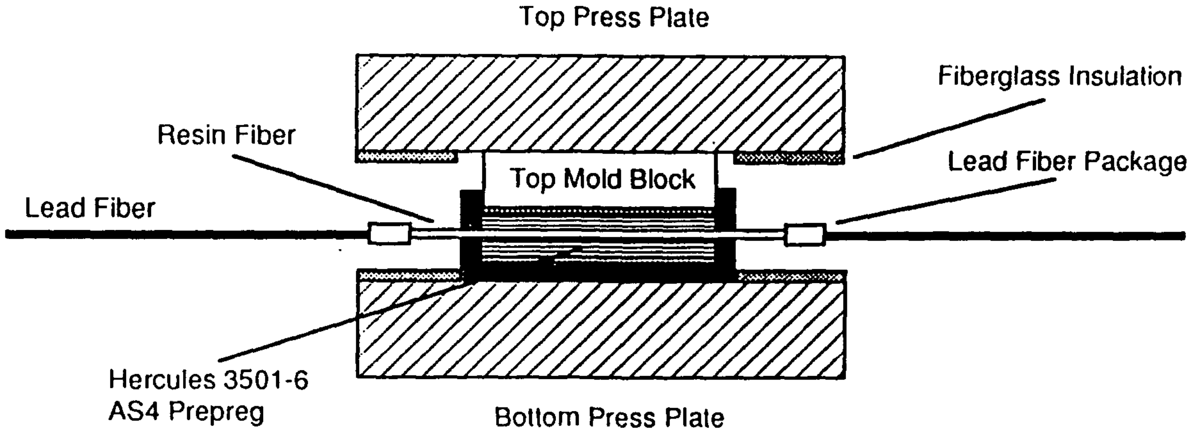

Figure 1: Crossection of the Hot Press Assembly Used for the Cure Monitoring Experiments.

3.2) Composite Coupon Fabrication/Cure Monitoring:

The coupon fabrication process was set up such that a preheat cycle lasting approximately 47 minutes (45 measurement intervals) was used to remove some of the air bubbles within the mold. The preheat temperature was approximately 125 °C at which the Hercules 3501-6 resin reaches its lowest viscosity prior to gelling. After the 45th measurement interval, temperature was increased to 180 °C for an additional 75 intervals (78 minutes) to cure the composite. Both during the preheat and cure cycle, the press plate temperatures would fluctuate by approximately +/- 5 °C about the set-point temperature.

Figure 2 shows a plot of the first real time, in-situ cure monitoring results (see Appendix A for tabulated results). A double-y graph is used with Normalized Transmitted Power (NTP = Psig/Pref) in W/W labeled on the left vertical axis, and temperature in °C labeled on the right vertical axis. The 125 and 180 °C cycles can clearly be identified from the dotted line, and temperature fluctuations of the press plates are evident. During the 125 ° C preheat cycle (first 45 intervals) the NTP decreases slowly due to some gelling in this period. The decrease in NTP during the preheat cycle, however, is relatively small compared to the exponential decay of NTP which occurs after the temperature is raised to 180 °C. After the 100th interval the decay in NTP seems to level off, indicating that the cure process is approaching its final stage. As proposed earlier, the decay in NTP is best evaluated by numerically differentiating Psig/Pref to obtain a plot of the rate of cure (see Figure 3). Although sporadic d(Psig/Pref) behavior is seen during the preheat cycle, a relatively smooth smooth curve is obtained during the actual cure cycle. This curve is especially smooth in the later intervals (60-120).during which a cure criterion could conceivably be assigned (see Figure 4). It is very possible that some of the "ripple" on top of the d(Psig/Pref) curve is due

to the fluctuation in cure temperature. In fact, it is known that Psig, the transmitted signal power through the resin fiber, is dependent on temperature. From the graph in Figure 2, for example, it can be seen that whenever temperature is increased, NTP increases as well until the set-point temperature has been reached. The quantified effect of the fluctuating temperature on the performance of the cure monitor must yet be determined.

3.3) Coupon Inspection Under a Microscope:

After completing the fabrication/cure monitoring process, the composite coupon was cut length-wise to obtain some information on the lay of the resin fiber within the coupon. After cutting the specimen length-wise, the cut surface was polished and inspected under a 40x microscope. As can be seen in Figure 5, the size of the resin fiber, which runs parallel to the graphite fibers, is relatively large causing what is hopefully only a resin rich area within the composite. This resin rich area can be reduced in size by going to a smaller resin fiber diameter (<100 μm) in the future. More important however will be the analysis of the resin fiber to cured composite resin bond. Obviously, it is hoped that the resin fiber will blend in with the composite resin such that this bond is extremely strong. A strong bond between the resin fiber and the cured composite resin will result in minimum degradation of composite strength characteristics. From Figure 5 one can also observe some air pockets (dark spots) which are not the result of embedding the resin fiber, but insufficient composite de-airing. Elimination of these air pockets is anticipated to be relatively trivial by applying more controlled precure/preheat conditions.

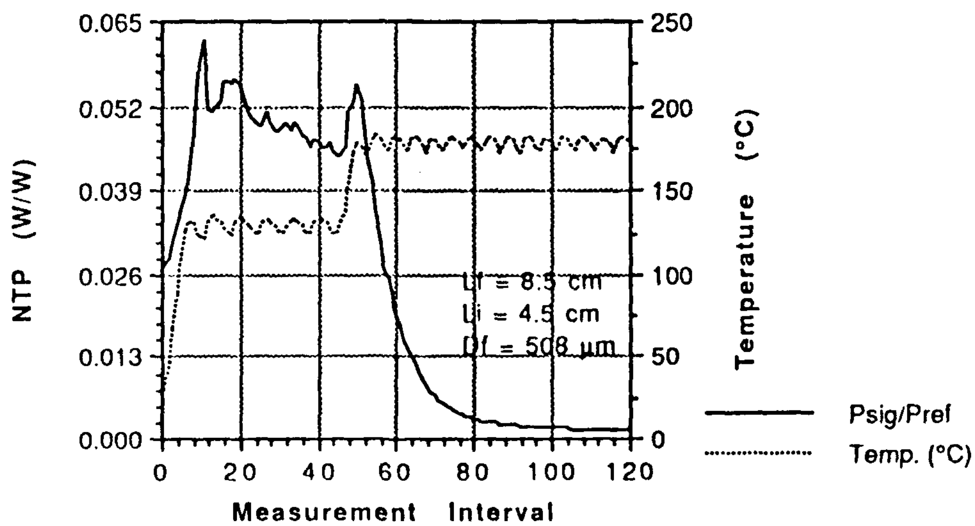

Figure 2: Normalized Transmitted Power (NTP) and Temperature Versus Measurement Interval.

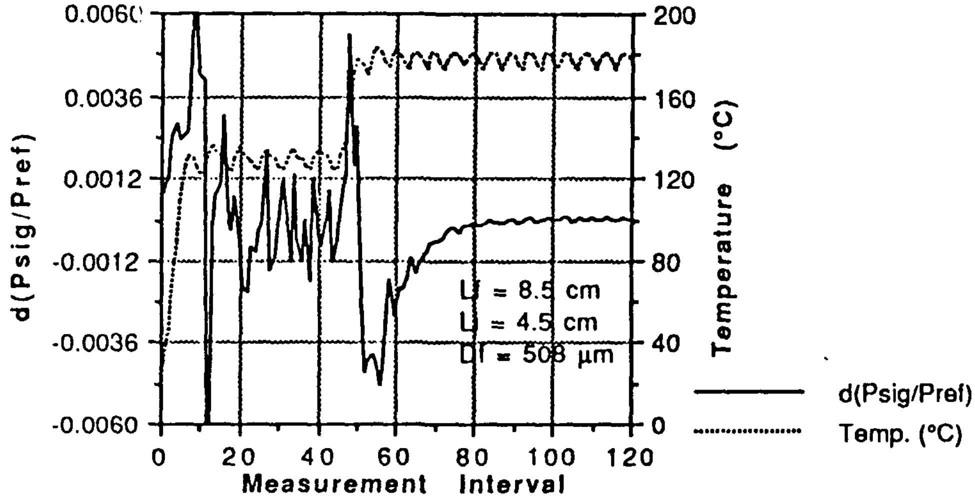

Figure 3: Numerical NTP Derivative and Temperature Versus Measurement Interval.

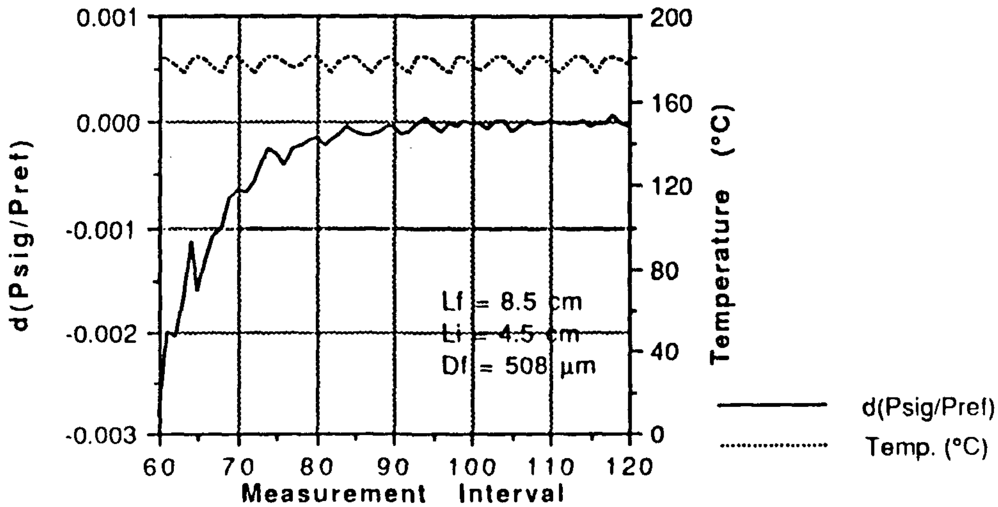

Figure 4: Numerical NTP Derivative and Temperature During the Later Part of the Cure.

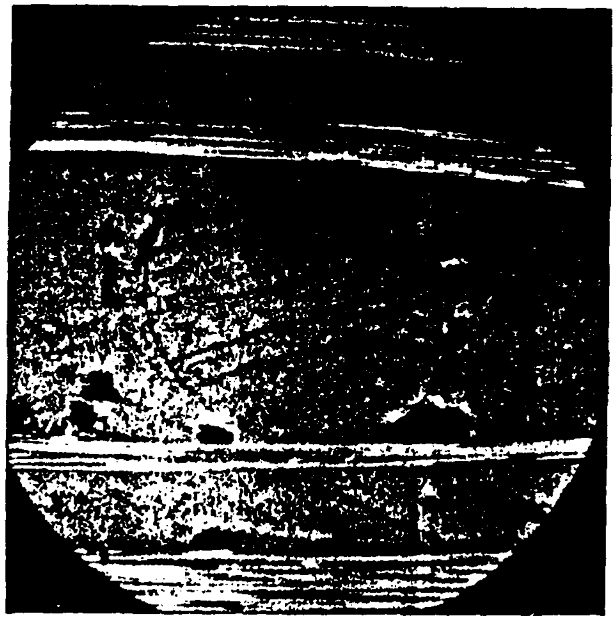

Figure 5: Photomicrograph of Embedded Resin Fiber Within Composite Specimen.

4.) UPCOMING TASKS/FOLLOW-UP EFFORTS:

The experimental results of this fifth month of the project have basically established the direction of future development regarding the proposed fiber optic cure monitor. Several crucial factors will have to be included and analyzed towards the end of this project and during subsequent Phase II follow-up efforts. Immediate suggestions for Phase II development, which will certainly be addressed in more detail in the final report and pending Phase II proposals, include a) neat resin preparation before resin fiber fabrication, b) improved resin fiber fabrication techniques, c) resin fiber embedding and interaction with the composite, d) interpretation of the monitor data and subsequent process control, e) impact of the cure monitor on composite characteristics, and f) use of the cure monitor for post cure process sensing applications.

4.1) Neat Resin Preparation:

The resin currently used for making the cure monitor resin fibers is standard grade Hercules 3501-6 resin material. The material, as currently received from the supplier, has not undergone any special purification treatment, nor has emphasis been placed on degassing/de-airing the material. Considering that in the future longer length (> 1 m) fibers may be needed, it will be necessary to look at techniques which will insure the highest optical transmission coefficients. With a typical monitoring system dynamic range of approximately 30 dB, and a maximum resin fiber length of, let's say 10 m, the loss of the resin material after purification and de-airing would have to be less than 3 dB/m. Whether such a low material loss is possible will have to be determined.

4.2) Resin Fiber Fabrication:

The methods currently used to fabricate the resin fibers are adequate for demonstration of feasibility. However limitations on minimum fiber diameter, maximum fiber length, and presence of fiber contaminants still exist. Since a mold technique is used to make the fibers, the removal of the fibers from the mold after curing becomes extremely difficult for fibers having a diameter of less than 300 µm. Removal, and also filling of the mold with the resin material currently limit the maximum achievable fiber length to approximately 15 cm. Handling of the cured resin fiber places contaminants on its surface, and can cause surface scratches which will negatively affect its transmission characteristics. It is therefore proposed to look at alternate fiber fabrication techniques. These include hollow capillary tube filling methods in conjunction with electrolysis or chemical etching for subsequent capillary tube removal. These methods are already being addressed in our labs and may provide the answer to making fibers with diameters < 100 µm and lengths > 1 m.

4.3) Resin Fiber Embedding:

Further focus on placement of the resin fiber within the composite is also proposed. As the fiber diameter decreases, proper placement to minimize fiber losses due to microbending will be necessary. At this point the fiber diameter is still large enough (508 µm) that microbending due to the pressure of the graphite fibers against the fiber surface is expected to be minimal. The effect of microbending however will become an issue as the diameter of the resin fiber approaches that of the composite graphite fibers. Special fiber lay-ups may be necessary to minimize microbending losses.

4.4) Process Control:

Once fully understood, the fiber optic cure monitor will provide cure state information which can be used to control the cure process. Complete understanding of the monitor includes establishing cure criteria for various fiber types, lengths, diameters, and resin types. Once these criteria exist, real time feedback loops can be implemented to adjust cure conditions accordingly. These conditions include cure pressure, temperature, and time all of which need to be optimized for an efficient, cost effective process.

4.5) Cure Monitor Impact on the Composite:

It is also advised to perform a detailed test program which will address the impact of the embedded resin fibers on composite coupon strength and fatigue. Once an optimum resin fiber/fiber lay-up combination has been determined, a rigorous test program should be conducted. This program

should include traditional tensile and flexural strength, as well as fatigue/aging testing. Emphasis will also be placed on resin fiber bonding to the composite, since it is expected to play a major role in not only preserving the integrity of the composite, but also in using the fiber for sensing applications after the composite is manufactured.

4.6) Post Cure Sensing Applications:

In the original SBIR solicitation an interest in using the embedded cure monitor for post cure process sensing applications was expressed. Preliminary composite coupon inspections in our laboratories indicate that this could be feasible; optical transmission loss of the resin fiber even after the cure process is completed seems to be low enough to allow visual detection of ambient, uncollimated light through a 4.5 cm wide specimen. This suggests that the embedded cure monitor fiber, which has already blended in with the composite structure, provides a light path for an optical probe signal at a particular wavelength. This light path can therefore be used to sense parameters during the lifetime of the composite. Such parameters include strain, temperature, and pressure.

5.) CONCLUSIONS:

During the fifth month of SBIR Phase I contract # DAAL04-90-C-0013 we have performed the first real time, in-situ cure monitoring experiment using Hercules 3501-6 AS4 composite prepreg material. The experiment indicates that the behavior of the embedded resin fiber within the composite behaves similarly to those fibers embedded in neat resin. Graphs of the numerical derivative of the Normalized Transmitted Power (NTP) versus time show that an absolute criterion may be placed on the cure state of the composite. Suggestions for follow-up efforts have also been presented.

6.) REFERENCES:

[1] FIMOD Corp.SBIR Phase 1 Proposal "Fiber Optic Sensors for In-Situ Process Measurements Within Organic Matrix Composite Materials", Dec. 29, 1990, pp. 8 - 14.

[2] FIMOD Corp. Monthly Technical Status Report (7/16/90 - 8/14/90) "Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring".

[3] FIMOD Corp. Monthly Technical Status Report (8/15/90 - 9/10/90) "Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring".

[4] FIMOD Corp. Monthly Technical Status Report (9/11/90 - 10/12/90) "Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring".

[5] FIMOD Corp. Monthly Technical Status Report (10/13/90 - 11/9/90) "Optical Fiber Sensors for Organic Matrix Composite Material Cure Monitoring".

	Interval	Psig	Pref	Psig/Pref	d(Psig/Pref)	Temp. (°C)
1	0	7.95e-7	3.02e-5	2.63e-2		26
2	1	8.17e-7	3.02e-5	2.71e-2	7.28e-4	30
3	2	8.57e-7	3.02e-5	2.84e-2	1.32e-3	46
4	3	9.27e-7	3.01e-5	3.08e-2	2.42e-3	67
5	4	1.01e-6	3.01e-5	3.36e-2	2.76e-3	89
6	5	1.08e-6	3.01e-5	3.59e-2	2.33e-3	108
7	6	1.15e-6	3.00e-5	3.83e-2	2.45e-3	126
8	7	1.23e-6	3.01e-5	4.09e-2	2.53e-3	131
9	8	1.43e-6	3.00e-5	4.77e-2	6.80e-3	130
10	9	1.62e-6	3.01e-5	5.38e-2	6.15e-3	125
11	10	1.74e-6	3.00e-5	5.80e-2	4.18e-3	123
12	11	1.86e-6	3.00e-5	6.20e-2	4.00e-3	121
13	12	1.54e-6	3.00e-5	5.13e-2	-1.07e-2	130
14	13	1.55e-6	3.03e-5	5.12e-2	-1.78e-4	136
15	14	1.56e-6	3.01e-5	5.18e-2	6.72e-4	133
16	15	1.59e-6	3.01e-5	5.28e-2	9.97e-4	131
17	16	1.68e-6	3.01e-5	5.58e-2	2.99e-3	128
18	17	1.67e-6	3.00e-5	5.57e-2	-1.47e-4	124
19	18	1.66e-6	3.00e-5	5.53e-2	-3.33e-4	123
20	19	1.68e-6	3.00e-5	5.60e-2	6.67e-4	130
21	20	1.66e-6	3.00e-5	5.53e-2	-6.67e-4	134
22	21	1.60e-6	3.00e-5	5.33e-2	-2.00e-3	132
23	22	1.54e-6	3.01e-5	5.12e-2	-2.17e-3	129
24	23	1.51e-6	3.00e-5	5.03e-2	-8.29e-4	128
25	24	1.48e-6	3.00e-5	4.93e-2	-1.00e-3	124
26	25	1.47e-6	3.00e-5	4.90e-2	-3.33e-4	124
27	26	1.47e-6	3.01e-5	4.88e-2	-1.63e-4	130
28	27	1.53e-6	3.01e-5	5.08e-2	1.99e-3	133
29	28	1.48e-6	3.00e-5	4.93e-2	-1.50e-3	131
30	29	1.45e-6	3.01e-5	4.82e-2	-1.16e-3	129
31	30	1.44e-6	3.01e-5	4.78e-2	-3.32e-4	126
32	31	1.47e-6	3.00e-5	4.90e-2	1.16e-3	124
33	32	1.48e-6	3.00e-5	4.93e-2	3.33e-4	127
34	33	1.46e-6	3.04e-5	4.80e-2	-1.31e-3	133
35	34	1.48e-6	3.00e-5	4.93e-2	1.31e-3	133
36	35	1.46e-6	3.00e-5	4.87e-2	-6.67e-4	130
37	36	1.42e-6	3.00e-5	4.73e-2	-1.33e-3	129
38	37	1.42e-6	3.00e-5	4.73e-2	0.00e+0	125
39	38	1.36e-6	2.99e-5	4.55e-2	-1.85e-3	124
40	39	1.40e-6	3.00e-5	4.67e-2	1.18e-3	130
41	40	1.38e-6	2.99e-5	4.62e-2	-5.13e-4	133
42	41	1.36e-6	3.00e-5	4.53e-2	-8.21e-4	132
43	42	1.36e-6	3.00e-5	4.53e-2	0.00e+0	131
44	43	1.39e-6	3.01e-5	4.62e-2	8.46e-4	128
45	44	1.35e-6	3.01e-5	4.49e-2	-1.33e-3	124
46	45	1.33e-6	3.01e-5	4.42e-2	-6.64e-4	124
47	46	1.34e-6	3.02e-5	4.44e-2	1.85e-4	131
48	47	1.37e-6	3.00e-5	4.57e-2	1.30e-3	138
49	48	1.53e-6	3.00e-5	5.10e-2	5.33e-3	154
50	49	1.58e-6	3.01e-5	5.25e-2	1.49e-3	171
51	50	1.65e-6	2.99e-5	5.52e-2	2.69e-3	178
52	51	1.58e-6	3.01e-5	5.25e-2	-2.69e-3	175
53	52	1.45e-6	3.02e-5	4.80e-2	-4.48e-3	172
54	53	1.32e-6	3.01e-5	4.39e-2	-4.16e-3	170
55	54	1.20e-6	3.01e-5	3.99e-2	-3.99e-3	180
56	55	1.07e-6	3.00e-5	3.57e-2	-4.20e-3	183

	Interval	Psig	Pref	Psig/Pref	d(Psig/Pref)	Temp. (°C)
57	56	9.19e-7	2.99e-5	3.07e-2	-4.93e-3	180
58	57	8.04e-7	3.00e-5	2.68e-2	-3.94e-3	177
59	58	7.48e-7	2.99e-5	2.50e-2	-1.78e-3	174
60	59	6.83e-7	3.00e-5	2.28e-2	-2.25e-3	179
61	60	6.02e-7	3.02e-5	1.99e-2	-2.83e-3	182
62	61	5.38e-7	3.00e-5	1.79e-2	-2.00e-3	179
63	62	4.78e-7	3.01e-5	1.59e-2	-2.05e-3	177
64	63	4.26e-7	3.00e-5	1.42e-2	-1.68e-3	173
65	64	3.93e-7	3.01e-5	1.31e-2	-1.14e-3	179
66	65	3.43e-7	3.00e-5	1.14e-2	-1.62e-3	181
67	66	3.04e-7	3.01e-5	1.01e-2	-1.33e-3	179
68	67	2.71e-7	3.01e-5	9.00e-3	-1.10e-3	175
69	68	2.40e-7	3.00e-5	8.00e-3	-1.00e-3	172
70	69	2.18e-7	3.00e-5	7.27e-3	-7.33e-4	180
71	70	2.00e-7	3.02e-5	6.62e-3	-6.44e-4	180
72	71	1.80e-7	3.02e-5	5.96e-3	-6.62e-4	177
73	72	1.62e-7	3.00e-5	5.40e-3	-5.60e-4	173
74	73	1.50e-7	3.03e-5	4.95e-3	-4.50e-4	177
75	74	1.41e-7	3.01e-5	4.68e-3	-2.66e-4	181
76	75	1.32e-7	3.01e-5	4.39e-3	-2.99e-4	180
77	76	1.20e-7	3.02e-5	3.97e-3	-4.12e-4	178
78	77	1.12e-7	3.02e-5	3.71e-3	-2.65e-4	175
79	78	1.05e-7	3.01e-5	3.49e-3	-2.20e-4	177
80	79	9.96e-8	3.01e-5	3.31e-3	-1.79e-4	181
81	80	9.57e-8	3.03e-5	3.16e-3	-1.51e-4	180
82	81	8.85e-8	3.02e-5	2.93e-3	-2.28e-4	177
83	82	8.30e-8	3.02e-5	2.75e-3	-1.82e-4	173
84	83	7.93e-8	3.02e-5	2.63e-3	-1.23e-4	178
85	84	7.77e-8	3.01e-5	2.58e-3	-4.44e-5	181
86	85	7.49e-8	3.01e-5	2.49e-3	-9.30e-5	180
87	86	7.11e-8	3.00e-5	2.37e-3	-1.18e-4	176
88	87	6.79e-8	3.02e-5	2.25e-3	-1.22e-4	172
89	88	6.51e-8	3.01e-5	2.16e-3	-8.56e-5	178
90	89	6.42e-8	3.02e-5	2.13e-3	-3.70e-5	181
91	90	6.28e-8	3.02e-5	2.08e-3	-4.64e-5	179
92	91	5.94e-8	3.02e-5	1.97e-3	-1.13e-4	175
93	92	5.64e-8	3.03e-5	1.86e-3	-1.06e-4	172
94	93	5.54e-8	3.01e-5	1.84e-3	-2.09e-5	180
95	94	5.62e-8	3.02e-5	1.86e-3	2.04e-5	181
96	95	5.50e-8	3.02e-5	1.82e-3	-3.97e-5	179
97	96	5.27e-8	3.04e-5	1.73e-3	-8.76e-5	175
98	97	5.14e-8	3.01e-5	1.71e-3	-2.59e-5	173
99	98	5.02e-8	3.02e-5	1.66e-3	-4.54e-5	180
100	99	5.04e-8	3.03e-5	1.66e-3	1.11e-6	180
101	100	4.99e-8	3.02e-5	1.65e-3	-1.10e-5	177
102	101	4.86e-8	3.00e-5	1.62e-3	-3.23e-5	174
103	102	4.67e-8	3.01e-5	1.55e-3	-6.85e-5	176
104	103	4.71e-8	3.01e-5	1.56e-3	1.33e-5	181
105	104	4.74e-8	3.01e-5	1.57e-3	9.97e-6	180
106	105	4.48e-8	3.02e-5	1.48e-3	-9.13e-5	176
107	106	4.39e-8	3.03e-5	1.45e-3	-3.46e-5	173
108	107	4.40e-8	3.01e-5	1.46e-3	1.29e-5	178
109	108	4.37e-8	3.02e-5	1.45e-3	-1.48e-5	181
110	109	4.31e-8	3.04e-5	1.42e-3	-2.93e-5	180
111	110	4.31e-8	3.01e-5	1.43e-3	1.41e-5	177
112	111	4.20e-8	3.00e-5	1.40e-3	-3.19e-5	173

	Interval	Psig	Pref	Psig/Pref	d(Psig/Pref)	Temp. (°C)
113	112	4.17e-8	3.02e-5	1.38e-3	-1.92e-5	176
114	113	4.13e-8	3.02e-5	1.37e-3	-1.32e-5	180
115	114	4.17e-8	3.02e-5	1.38e-3	1.32e-5	180
116	115	4.04e-8	3.00e-5	1.35e-3	-3.41e-5	177
117	116	4.02e-8	3.02e-5	1.33e-3	-1.55e-5	172
118	117	3.98e-8	3.03e-5	1.31e-3	-1.76e-5	179
119	118	4.08e-8	3.00e-5	1.36e-3	4.65e-5	181
120	119	4.06e-8	3.02e-5	1.34e-3	-1.56e-5	179
121	120	3.94e-8	3.01e-5	1.31e-3	-3.54e-5	177